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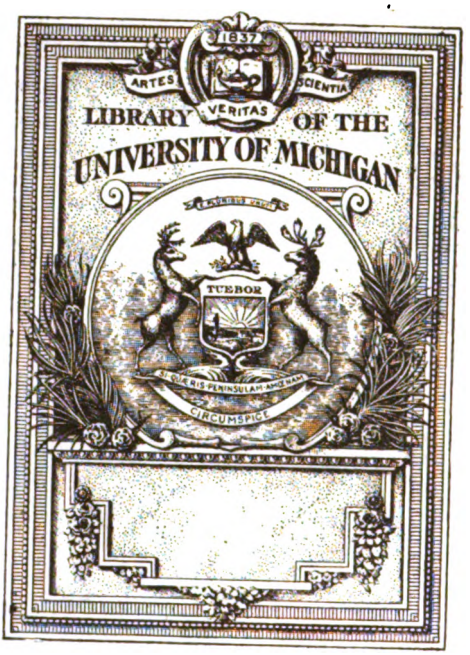

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INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.*

On account of the difficulties of correspondence between its

INTERNATIONAL ATOMIC WEIGHTS, 1917.

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulfur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	88.7
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

* *Journal of the American Chemical Society*, Dec. 1917.

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members, due to the war, the International Committee on Atomic Weights has decided to make no full report for 1918. Although a good number of new determinations have been published during the past year, none of them seems to demand any immediate change in the table for 1917. That table, therefore, may stand as official during the year 1918.

F. W. CLARKE,
Chairman.

TANNIN CONTENT OF PACIFIC COAST TREES.*

By H. K. Benson and Frank M. Jones.

In a previous article it was shown[1] that the tannin content of Douglas fir slabwood when properly selected contained sufficient tannin to be considered a suitable raw material for the extract industry. In order to ascertain what other species common to the Pacific Northwest might be available for extract manufacture this study was undertaken.

The samples in each case were taken from four or five trees of the same species, were first chipped in a Mitts & Merrill "hog," carefully quartered and the final sample finely ground in a Koerner drug mill. The extractor was of the same type as used in the previous study, extraction carried on for 16 hours and analyzed according to the method of the American Leather Chemists' Association (1914). All calculations are made on a moisture-free basis.

The sample of sawmill slab reported in the previous study (*l. c.*) was still available, having been kept in a loosely stoppered jar. It was thought of interest to ascertain its tannin content after a year's storage. The average of seven analyses is given in Table I for comparison with previous results.

From these results, it would seem that the effect of seasoning is to bring about hydrolysis and possibly oxidation, thereby increasing the tannin content by 1.6 per cent. (27 per cent. of the former). The total solids are increased and the non-tannin decreased, each 0.9 per cent.

* *Journal of Ind. and Eng. Chem.*, Dec., 1917.

[1] *J. I. & E. C.*, 7, 1915.

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TABLE I.—EFFECT OF SEASONING ON TANNIN CONTENT OF DOUGLAS FIR.

Percentages	Fir Slabwood analyzed by Thompson in 1914	Same sample analyzed by Jones one year later
Total solids	14.92	15.8
Soluble solids	13.02	13.7
Reds	1.90	2.1
Non-tannins	7.10	6.2
Tannins	5.92	7.5
Moisture	6.91	10.0

PART I—CONIFERS.

WESTERN LARCH (*Larix Occidentalis.*)—The sample was taken from four trees, averaging 28 inches in thickness, growing in the Whitman National Forest in Oregon. The trees were felled in December, 1910, and transported by skidding and log train to the station. The cross-sections were cut 18 inches from the ground and showed a very wet and pitchy surface. The wood is dull red in color and the bark averaged 2¼ inches in thickness. The sample was dried for one week at 40° C. before extraction. The analyses were made in March, 1916.

The tannin content of this, as well as of the other species tested, is given in Table II.

The wood extract was bright red in color and unimportant from the standpoint of either tannin content or dye. The extract from the bark was a dull red and gave a pleasing light red color to the tanned hide.

Inasmuch as this species ranks ninth in the order of most prevalent trees in the states of Oregon and Washington, often occurring in pure forests in Northeastern Washington, Northern Idaho, and Northwestern Montana, is a prolific seeder and well adapted to reforest burned-over areas, its importance as a source of tannin must not be overlooked. Investigations carried on in the U. S. Forest Products Laboratory also show[2] that this species produces a high yield of alcohol by hydrolysis.

Considering the high tannin content of its bark and the exceptional yield of alcohol, it would seem that this species might be especially adapted to chemical utilization, rather than for lumber and timber purposes.

[2] *This Journal*, 7, (1915), 922.

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TABLE II.—TANNIN CONTENT OF PACIFIC COAST SPECIES.

Percentages		Total solids	Soluble solids	Reds	Non-tannins	Tannins	Moisture
Western Larch	Wood (*a*) ...	28.9*	27.6*	None*	23.9*	6.7*	7.8*
	Bark (*b*)	20.5	17.0	3.5	6.4	10.6	11.0
Western Yellow Pine	Wood (*c*)....	19.6	16.9	2.7	8.0	8.9	....
	Bark (*c*)	22.3	19.3	3.1	8.3	10.9	4.0
Western Hemlock	Wood (*c*) ...	4.2	4.1	0.1	3.1	1.0	9.5
	Bark (*c*).....	20.8	19.5	1.3	8.57	10.93	9.8
Dogwood	Wood	8.3	7.1	1.2	5.8	1.3	5.0
	Bark	8.3	7.9	0.4	6.2	1.7	5.0
Cottonwood	Wood	10.8	9.1	1.7	7.3	1.8	6.5
	Bark	25.3	24.3	1.0	19.6	4.7	2.0
Alder	Wood	3.5	3.3	0.2	2.6	0.7	6.8
	Bark	10.2	9.6	0.6	6.2	3.3	9.8

(*a*) Results are averages of 2 extractions. *Analysis by W. E. Gailey.
(*b*) Results are averages of 8 extractions.
(*c*) Results are averages of 4 extractions.

YELLOW PINE (*Pinus Ponderosa.*)—This sample was obtained from the Whitman National Forest, the cross-sections being cut 18 inches in diameter. The bark averages 2 inches in thickness. The trees were felled 4 months before extraction.

This species ranks second in quantity of the standing timber of Oregon and Washington. The bark on old trees is often 3 to 4 inches thick. The yellow pine is chiefly used in making boxes, but both the quantity of the bark and of the tannin in the bark and wood make the use of the sawmill waste of this species feasible for tannin extract manufacture.

WESTERN HEMLOCK (*Tsuga Heterophilla.*)—Various published analyses of the western hemlock bark show that the tannin content of the western species is equal to or exceeds that of the eastern species. The bark of the western hemlock has been regularly used by tanneries on the Pacific Coast. Inasmuch as considerable second growth hemlock occurs on the logged off lands of the Northwest, a composite sample of four trees taken from the University campus was prepared. One tree was 18 inches in diameter and the other three averaged 9 inches. The bark was ½ inch thick. The trees were felled 9 months before extraction. The tannin content is less than that found by other investigators, due probably to the difference in the ages of the trees.

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PART II—DECIDUOUS SPECIES.

DOGWOOD (*Cornus Nuttalli.*)—The western dogwood is essentially the same as that of the East. The wood is a dull pink and the bark a reddish black. Its dye possibilities have been utilized by the Pacific Coast Indians for coloring clothing and moccasins deep red. It ranges from the southern coast of British Columbia through Washington, Oregon and California, usually thriving in low altitudes and damp soils and mixed singly or in groups under all the trees of the Pacific slope except the yellow and sugar pines.

For the sample, cross-sections of five trees on the university campus were cut 3 feet from the ground. They ranged from 8 to 24 inches in diameter, and were air-dried for 6 months. The bark averaged less than ½ inch in thickness and was not easily peeled. The extract is reddish brown in color and imparts a light reddish brown color to the tanned hide in the case of the wood extract and a deeper red from the bark. It is believed that dogwood extract might be used with other tanning extracts to furnish the dye property.

COTTONWOOD (*Populis Trichocarpa.*)—The cottonwood tree is found growing in damp, sandy land from Alaska to Mexico. It is a very rapid grower, a tree growing to 15 inches in as many years. The sample was obtained from a tree 2 feet in diameter, felled 3 months before extraction. The bark ranged from ½ to ¾ inches in thickness.

ALDER (*Alnus Oregona.*)—This species occurs to a considerable extent as a second growth on the logged off lands of Oregon and Washington. Four trees were cut on the university campus 9 months before extraction. Cross-sections were taken about 2 feet from the ground. The average diameter of the tree was 10 inches, the bark averaging ¼ inch in thickness. The quality of the tannin is of doubtful value.

CONCLUSIONS.

I. Douglas fir slabwood, selected for tanning extraction, can advantageously be seasoned for one year.

II. In addition to the western hemlock bark, that of the

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western larch and western pine seems to yield extract satisfactory both in quantity and quality.

III. Of the deciduous species examined, the dogwood alone appears suitable for use in extract manufacture but only as a dye.

THE DETERMINATION OF ASH IN LEATHER.

By Oskar Riethof and C. T. Gayley.

In looking over the reports of leather analyses printed in the Journals of the *A. L. C. A.*, and from other sources, we note great variations in the insoluble ash figure, and in as much as it is an established fact that the insoluble ash rarely exceeds 0.25 per cent. in leathers not weighted with insoluble materials such as barium sulphate, lead sulphate, kaolin, etc., it would seem that the higher values are often occasioned by wrong methods of determination. An error in the insoluble ash figure itself is not of great consequence, but it will cause an appreciable error in the combined tannin figure, and consequently in the "Degree of Tannage." It would, therefore, seem advisable to incorporate in the Official Method of leather analysis, a specific way for determining the ash.

Parker and Paul[1] believed that Schroeder's method of leather analysis had the error of calculating the soluble ash twice; once in his ash figure, and again in his soluble non-tannins. Paessler[2], one of the collaborators of Schroeder, replied that Schroeder always specified "Organic Solubles," and that his ash figure was really the total ash. Veitch and Rogers[3], in their tables of leather analyses, took for granted that, according to Parker's figures, sole leather not weighted with incombustible, insoluble material, never shows more than 0.3 per cent. insoluble ash, and they used this figure in determining the combined tannin. Some anonymous English writer in the *Leather Trades Review*, Nov. 10, 1915[4], gives the insoluble ash of three English and four American sole leathers between 0.36 per cent. and 0.90 per cent. Such high results, especially in American leathers, would seem

[1] *Jour. Soc. Chem. Ind.*, 1910, *Jour. A. L. C. A.*, 1910, p. 305.
[2] *Collegium* 1910, No. 423, *Jour. A. L. C. A.*, 1910, p. 467.
[3] *Bulletin of Dept. of Agr.*, *Jour. A. L. C. A.*, 1913, p. 275.
[4] *Jour. A. L. C. A.*, 1916, p. 15.

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only to be caused by improper analytic methods, since these leathers were not weighted with inorganic insoluble materials.

The present Official Method does not specify anything on the subject, but most chemists report "Insoluble Ash," and their figure for soluble non-tannin therefore includes the soluble ash. Others, like von Schroeder, report "Total Ash" and "Organic Soluble Non-tannin." Both ways are justified, but the first seems preferable, because uncombined tannin and soluble non-tannin give the water solubles, and there is no reason why the water solubles should not contain the soluble mineral matter. Above all, it is certainly wrong to give the soluble ash twice, first in the total ash and again in the soluble non-tannin.

Different methods for determining the total, soluble, and insoluble ash are in use. The official method of the *A. L. C. A.* for total ash is to incinerate from 10 to 15 grams of the sample. Procter[5] advises the use of 5 grams for the purpose, which according to our belief is more than sufficient. In case the soluble ash is not dissolved out after charring, and before the ignition is completed, this figure will be too low when much Epsom salts is present, on account of loss of SO_3. The insoluble ash may be found by igniting a part of the extracted leather, after it is dried. The soluble ash may be found by ashing the total solids from the water solubles. The last two figures combined should correspond with the total ash, but in many cases do not, because in the presence of sulphates the total ash figure will be too low on account of reduction of the sulphates by the carbon, and the loss of SO_3, as pointed out above. We found that the soluble ash determined as above was in many cases considerably higher than the total ash, depending on the intensity and duration of the ignition.

It is very probable that the method some chemists use in determining the insoluble ash is to wash the total ash out with hot water, to filter off, and again ignite the insoluble part. This will certainly give results too high in most cases, and especially when magnesium sulphate is present, which will be partly converted into insoluble magnesia by ignition. We would not be surprised to find this the reason for the high insoluble ash figures of the English chemist mentioned above.

[5] *Leather Chemists Pocket-book.*

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In view of the foregoing facts, we think it advisable for the association to adopt a specific way of reporting leather analyses, and furthermore, incorporate in the Official Method a certain way of determining insoluble, soluble and total ash. The method we would suggest for determining the insoluble ash is that of ashing a part of the dried leather substance. The total ash may either be obtained by ashing the total solids from the water solubles, and adding this figure to the insoluble ash, or by ashing a part of the original sample. It would seem that the first way mentioned would be the easier, and should give results nearer the truth.

COMPARATIVE EXTRACT ANALYSIS.

By J. M. Seltzer.

In the purchase of extract for our tanneries, it is our custom to receive a portion of the sample drawn by the manufacturer at his plant and the manufacturer also sends a portion of the sample to his own laboratory or to that of an independent chemist.

When the car of extract is received at our tanneries, we draw a sample and send a portion to the manufacturer and we retain a portion of the sample for our own laboratory.

We give below, the tannin contents of 100 tanks of extract bought from one manufacturer. These figures show the tannin found by the manufacturers' chemist on the manufacturers' and tannery sample, and also the tannin found by the tannery chemist on the manufacturers' and tannery sample.

Chemist A is the tannery chemist.

Chemist B is the manufacturers' chemist.

As will be noted, the greatest difference on the average of the 100 analysis is 0.07 per cent. tannin.

The average results of the two lots by Chemist A is 26.375 per cent.; the average results of the two lots by Chemist B is 26.34 per cent. The difference being 0.035 per cent. tannin which has a value of $42.00 on the 100 tanks, and by averaging the results of Chemist A and Chemist B, the difference between the average and the result of Chemist B would be $21.00 on the 100 tanks, which is 0.18 per cent. of the value of the extract.

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Manufacturer's Sample		Tannery Sample		Manufacturer's Sample		Tannery Sample	
Chemist A Tannin %	Chemist B Tannin %	Chemist A Tannin %	Chemist B Tannin %	Chemist A Tannin %	Chemist B Tannin %	Chemist A Tannin %	Chemist B Tannin %
25.46	25.57	25.30	25.51	26.18	26.03	25.92	25.94
26.38	26.34	26.46	26.35	26.89	26.81	27.01	26.78
26.15	26.12	25.98	26.20	26.50	26.98	26.61	26.92
24.53	24.70	24.66	24.78	26.35	26.58	26.45	26.49
25.84	25.53	25.65	25.46	25.70	25.59	25.80	25.62
25.78	25.59	25.87	25.68	26.46	26.31	26.66	26.39
24.98	24.62	25.06	24.77	26.57	26.62	26.54	26.52
26.12	25.96	26.21	25.96	25.93	25.52	25.90	25.60
26.31	26.12	26.44	26.13	26.59	26.87	26.93	26.83
25.88	25.53	25.85	25.51	27.08	27.15	27.33	27.33
26.57	26.57	26.44	26.38	26.08	26.17	26.31	26.27
26.13	26.02	26.11	26.00	27.43	26.84	27.26	26.89
26.16	25.73	26.20	25.73	27.30	26.75	27.17	26.92
27.11	27.01	27.40	27.13	27.23	27.07	27.34	27.16
27.01	26.71	26.60	26.19	27.35	27.18	27.30	27.35
27.44	27.06	27.37	26.94	27.27	27.04	27.19	27.10
28.25	27.85	27.88	27.77	27.31	27.59	27.49	27.40
27.18	27.09	26.80	27.14	26.87	26.76	27.01	26.65
27.77	27.70	27.73	27.68	26.96	27.08	26.99	26.94
26.23	26.09	26.30	26.11	27.04	26.56	26.89	26.79
26.23	26.14	26.25	26.21	26.85	26.70	26.97	26.79
26.48	26.51	26.62	26.49	26.64	26.25	26.66	26.29
26.59	26.53	26.49	26.15	26.67	26.65	26.74	26.55
26.05	26.12	26.17	26.06	26.99	27.08	26.90	27.05
26.75	26.39	26.68	26.44	26.68	26.71	26.63	26.82
25.93	25.40	25.61	25.43	26.07	26.35	26.42	26.45
26.25	25.95	26.03	25.97	26.05	26.20	26.74	26.58
26.20	25.99	26.56	26.13	26.36	26.38	26.51	26.56
26.80	26.89	26.67	26.93	26.85	27.07	26.74	26.80
26.04	26.13	26.37	26.40	26.55	26.45	26.74	26.55
26.43	26.52	26.48	26.56	27.03	27.13	27.34	27.19
26.09	26.30	26.14	26.32	26.35	26.13	26.14	26.23
26.18	26.02	26.04	26.29	25.51	25.83	25.58	25.68
26.51	26.51	26.36	26.64	25.15	25.36	25.29	25.65
26.65	26.79	26.57	26.85	25.63	25.57	25.72	25.62
25.41	25.32	24.97	25.25	25.00	24.87	25.32	25.23
25.35	25.42	25.66	25.47	26.51	26.56	26.56	26.64
25.85	25.88	25.75	25.85	25.36	25.05	25.70	25.63
25.85	25.86	25.62	25.68	25.43	25.42	25.52	25.60
26.74	26.98	26.90	27.00	25.86	25.56	26.02	25.84
26.94	26.85	26.79	26.85	25.55	25.39	25.55	25.31
26.92	26.98	26.81	27.26	25.70	25.67	25.47	25.59
26.40	26.64	26.38	26.57	26.36	26.23	26.76	26.49
27.35	27.39	27.57	27.60	25.79	26.04	26.32	26.09
26.11	26.28	26.23	26.42	25.90	25.62	25.84	25.89
26.51	26.73	26.36	26.68	26.03	26.01	26.29	26.13
26.23	26.28	26.19	26.31	26.04	26.27	25.93	26.19
26.56	26.75	26.42	26.54	25.85	26.40	25.80	26.26
26.66	27.05	26.56	27.01				
26.64	27.12	26.58	27.11	263608	263241	263885	263598
26.09	26.08	26.17	26.11	26.36	26.32	26.39	26.36
26.16	26.25	26.24	26.39				

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By looking over the above table it will be noticed that the analyses of each individual tank do not always agree, which can easily be accounted for by one who is familiar with the method of analysis. When a party buys only a few tanks of extract the difference is liable to run all one way and the most satisfactory method of settlement which would be fair to both buyer and seller would be to settle on the average tannin found by the seller's chemist on the sample taken by the seller, and the tannin found by the buyer's chemist on the sample taken by the buyer. In this way the tan contents of each and every tank of extract would be adjusted automatically and the transaction would be closed, and at the same time both parties would have the opportunity of drawing the samples and making the analyses.

LABORATORY, KISTLER, LESH & COMPANY.

LEATHER CONSERVATION.

By Allen Rogers.

Read before the New York Section of the American Chemical Society.

During the past ten years there has been a slow but constant falling off in hides and skins, which has resulted in a gradual decrease in the production of leather. This shortage in raw stock, with the increased demand for leather products has thus caused a rise in price of all classes of leather. This country has depended very largely upon European markets for its hides and skins, consequently with this source cut off, due to embargo and non-production, the prices have taken extraordinary bounds. To add to the seriousness of the situation, we find ourselves confronted with a shortage in domestic beef animals, and not having an adequate merchant marine, we are unable to reach the South American markets where large quantities of hides and skins are available.

This condition of affairs is deplorable, especially as the United States leads the world in the production of leather. What cannot be cured, however, must be endured. Although conditions in the leather trade are not so serious as they were a year or so ago, we must use every effort to conserve our resources and

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patiently await the day when a more efficient marine service will bring the markets of the world to our doors.

As the price of any commodity rises, substitutes are bound to appear. This has been true in the case in hand. Not only have leather substitutes been brought forward, but sources of raw material, formerly waste products, have come to the attention of the tanners, and are being worked up into merchantable leather. Processes also are now being employed which aim to produce a leather having a greater wearing quality than in previous years. Some of the processes are not new, but at the time they were proposed did not meet with favor by the trade. The reason for the lack of interest was due to the fact that the supply of hides was more plentiful than to-day and tanners did not care to change the process to conform to the new method.

In 1911, the speaker, working in conjunction with another member of this Section, developed a method for producing an indestructible sole leather. This leather was tested out on twenty mail carriers and twenty policemen in New York, using it on the right foot with the best oak sole on the left foot. Two oak soles went through and in most cases they were on the third before the new leather wore out. Shoe manufacturers and tanners did not seem interested at that time, but within the past two years several concerns have started to make the leather and it is now being advertised quite extensively.

The skins of fish have been tanned for many years, but only for fancy articles. To-day, however, shark skins, porpoise, and even gray fish, and eel skins are being converted into very serviceable leather. The shark skins have a very hard grain, but the flesh side lends itself to a finish which bids fair to make it a close competitive of box calf or oil grain. Shark skin leather is very tough and serviceable, which makes it well adapted for children's shoes, especially for boys' knockabouts. Gray fish and eel skins are thin, but can be used for fancy leather and small articles.

For many years the waste shavings and trimmings were burnt under the boiler. To-day, however, they are saved by mixing with pulp and put into leather board for insole work.

A recent invention proposes to work up small trimmings from light leather into a thread or yarn, and then use this yarn in

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weaving leather fabric. Such fabrics may be used for furniture, automobile leather, rugs, and fancy articles.

The heads or pates of hides formerly went into glue stock; to-day, however, these are being tanned and can be bought in the "Five and Ten" as half-soles and heels at 10 cents a pair.

In the production of automobile leather, the hide is cut up into sections or splits. As a hide can have only one grain side, the other cuts or splits are treated with a dope finish consisting of gun cotton and castor oil, to which a pigment is added. These splits are then embossed and given the appearance of a full grain.

The manufacture of imitation leather is an American idea and has developed into an enormous industry in recent years. This product consists of a fabric to which is applied a dope finish, the same as on splits. The fabric is then embossed and when used on upholstery is difficult to tell from real leather.

A new process has just been invented for making imitation leather, in which cotton batting takes the place of the fabric. This cotton is worked into shape on a felting machine, and then with a suitable binder is pressed into sheets. These sheets are then given a dope finish and embossed. This process is of special interest as the cost of the finished product is less than the cost of the fabric used in the older process. The strength also is far greater than leather or the other imitation leather.

For a number of years we have known and used rubber soles. Recently, however, several sole leather substitutes have been placed on the market under various trade names. These sole leather substitutes depend upon rubber for the binding material, but differ from the rubber sole in that they contain loading material and fibrous matter. Although they do not wear as well as high grade leather, they do have many points of value which should warrant consideration. Coming as they do when leather is short, they have served to tide us over a very serious situation and will continue to serve as a very timely and satisfactory adjunct to our sole leather supply.

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TENTATIVE STANDARD METHODS FOR THE SAMPLING AND ANALYSIS OF COMMERCIAL FATS AND OILS, OTHER THAN THOSE OF THE COCONUT, BUTTER AND LINSEED GROUPS.

The following methods have been adopted by the *Committee on the Analysis of Commercial Fats and Oils* of the *Division of Industrial Chemists and Chemical Engineers* of the American Chemical Society as tentative standards for the use of the trade, pending their official adoption by the American Chemical Society.

They are the result of thirty months continuous and conscientious effort on the part of the Committee and they have given excellent satisfaction in the hands of the members of the Committee and others who have used them, and have been found to answer the commercial needs of the fat and oil industry in a satisfactory manner.

They are published here for the purpose of adoption by any contracting parties so desiring and for the purpose of eliciting suggestions and criticisms from fat and oil chemists. Communications on the subject of the methods should be addressed to W. D. Richardson, c/o Swift & Company, Chicago, and will be presented to the Committee at their regular monthly meeting next following.

The Committee is now working on methods designed to apply particularly to the coconut, butter and linseed groups, and these methods, when adopted by the Committee, will include saponification number, iodine number and Reichert-Meissl number. When completed they will be incorporated in the methods printed below.

TENTATIVE STANDARD METHODS FOR THE SAMPLING OF COMMERCIAL FATS AND OILS.

Adopted September 22, 1916.

Any or all of the following tentative standard methods may be used or inserted in contracts at the option of the parties concerned.

Tank Cars.

1. SAMPLING WHILE LOADING.—Sample shall be taken at dis-

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charge end of pipe where it enters tank car dome. The total sample taken shall be not less than 50 pounds and shall be a composite of small samples of about 1 pound each, taken at regular intervals during the entire period of loading.

The sample thus obtained is thoroughly mixed and uniform 3-pound portions placed in air-tight 3-pound metal containers. At least three such samples shall be put up, one for the buyer, one for the seller and the third to be sent to a referee chemist in case of dispute. All samples are to be promptly and correctly labeled and sealed.

2. SAMPLING FROM CAR ON TRACK[1].—(*a*) *When Contents are Solid.*[2] In this case the sample is taken by means of a large tryer measuring about 2 inches across and about one and one-half times the depth of the car in length. Several tryerfuls are taken vertically and obliquely toward the ends of the car until 50 pounds are accumulated, when the sample is softened, mixed and handled as under (1).

(*b*) *When Contents are Liquid.*—The sample taken is to be a 50-pound composite made up of numerous small samples taken from the top, bottom and intermediate points by means of a bottle or metal container with removable stopper or top. This device, attached to a suitable pole, is lowered to the various desired depths, when the stopper or top is removed and the container allowed to fill. The 50-pound sample thus obtained is handled as under (1).

(*c*) *When Contents are in Semi-solid Conditions, or, When Stearine has Separated From Liquid Portions.*—In this case a combination of (*a*) or (*b*) may be used, or, by agreement of the parties, the whole may be melted and procedure (*b*) followed.

Barrels, Tierces, Casks, Drums, and Other Packages.

All packages shall be sampled, unless by special agreement the parties arrange to sample a lesser number; but, in any case, not less than 10 per cent. of the total number shall be sampled.

[1] Live steam must not be turned into tank cars or coils before samples are drawn, since there is no certain way of telling when coils are free from leaks.

[2] If there is water present under the solid material, this must be noted and estimated separately.

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The total sample taken shall be at least 20 pounds in weight for each 100 barrels, or equivalent.

1. BARRELS, TIERCES AND CASKS.—(*a*) *When contents are Solid.* The small samples shall be taken by a tryer through the bung-hole or through a special hole bored in the head or side for the purpose, with a 1-inch or larger auger. Care should be taken to avoid and eliminate all borings and chips from the sample. The tryer is inserted in such a way as to reach the head of the barrel, tierce, or cask. The large sample is softened, mixed and handled according to tank cars (1).

(*b*) *When Contents are Liquid.*—In this case use is made of a glass tube with constricted lower end. This is inserted slowly and allowed to fill with the liquid, when the upper end is closed and the tube withdrawn, the contents being allowed to drain into the sample container. After the entire sample is taken it is thoroughly mixed and handled according to tank cars (1).

(*c*) *When Contents are Semi-solid.*—In this case the tryer or a glass tube with larger outlet is used depending on the degree of fluidity.

(*d*) *Very Hard Materials, Such as Natural and Artificial Stearines.*—By preference the barrels are stripped and samples obtained by breaking up contents of at least 10 per cent. of the packages. This procedure is to be followed also in the case of cakes shipped in sacks. When shipped in the form of small pieces in sacks they can be sampled by grab sampling and quartering. In all cases the final procedure is as outlined under tank cars (1).

2. DRUMS.—Samples are to be taken as under (1), use being made of the bung hole. The tryer or tube should be sufficiently long to reach to the ends of the drum.

3. OTHER PACKAGES.—Tubs, pails and other small packages not mentioned above are to be sampled by tryer or tube (depending on fluidity) as outlined above, the tryer or tube being inserted diagonally whenever possible.

4. MIXED LOTS AND PACKAGES.—When lots of tallow or other fats are received in packages of various shapes and sizes, and especially wherein the fat itself is of variable composition, such must be left to the judgment of the sampler. If variable, the

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contents of each package should be mixed as thoroughly as possible and the amount of the individual samples taken made proportional to the sizes of the packages.

TENTATIVE STANDARD METHODS FOR THE ANALYSIS OF COMMERCIAL FATS AND OILS, OTHER THAN THOSE OF THE COCONUT, BUTTER AND LINSEED GROUPS.

Adopted September 22, 1916.

Sample.

The sample must be representative and at least 3 pounds in weight and taken in accordance with the standard methods for the sampling of commercial fats and oils (given above). It must be kept in an air-tight container in a dark, cool place.

Soften the sample by means of a gentle heat taking care not to melt it. When sufficiently softened, mix the sample thoroughly by means of a mechanical egg beater or other equally effective mechanical mixer.

Moisture and Volatile Matter.

APPARATUS: *Vacuum Oven.*[3]—The Committee Standard Oven.

Moisture Dish.—A shallow glass dish, lipped, beaker form, approximately 6 to 7 centimeters diameter and 4 centimeters deep shall be standard.

DETERMINATION.—Weigh out 5 grams (±0.2 gram) of the prepared sample into a moisture dish. Dry to constant weight *in vacuo* at a uniform temperature, not less than 15° C., nor more than 20° C. above the boiling point of water at the working pressure, which must not exceed 100 millimeters of mercury.[4] Constant weight is attained when successive dryings for 1-hour

[3] The diagram of this oven is shown in the original paper.

[4] BOILING POINT OF WATER AT REDUCED PRESSURES.

Pressure mm. Hg.	Boiling Point to 1° C.	Boiling Point +15° C.	Boiling Point +20°C.
100	52° C.	+67° C.	+72° C.
90	50	65	70
80	47	62	67
70	45	60	65
60	42	57	62
50	38	53	58
40	34	49	54

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periods show an additional loss of not more than 0.05 per cent. Report loss in weight as moisture and volatile matter.[5]

Suggestion for Routine Control Work.

The Following Method is Suggested by the Committee for Routine Control Work:—Weigh out 5- to 25-gram portions of prepared sample into a glass or aluminum[6] beaker or casserole and heat on a heavy asbestos board over burner or hot plate, taking care that the temperature of the sample does not go above 150° C. at any time. During the heating rotate the vessel gently on the board by hand to avoid sputtering or too rapid evolution of moisture. The proper length of time of heating is judged by absence of rising bubbles of steam, by the absence of foam or by other signs known to the operator. Avoid overheating of sample as indicated by smoking or darkening. Cool in desiccator and weigh.

Insoluble Impurities.

Dissolve the residue from the *moisture and volatile matter* determination by heating it on a steam bath with 50. cc. of kerosene. Filter the solution through a Gooch crucible properly prepared with asbestos,[7] wash the insoluble matter five times with 10-cc. portions of *hot* kerosene, and finally wash the residual kerosene out thoroughly with petroleum ether. Dry the crucible and contents to constant weight as in the determination of moisture and volatile matter and report results as insoluble impurities.

Soluble Mineral Matter.

Place the combined kerosene filtrate and kerosene washings from the insoluble impurities determination in a platinum dish. Place in this an ashless filter paper folded in the form of a cone, apex up. Light the apex of the cone, whereupon the bulk of

[5] Results comparable to those of the Standard Method may be obtained on most fats and oils by drying 5-gram portions of the sample, prepared and weighed as above, to constant weight in a well constructed and well ventilated air oven held uniformly at a temperature of 105 to 110° C. The thermometer bulb should be close to the sample. The definition of constant weight is the same as for the Standard Method.

[6] *Caution:* Aluminum soap may be formed.

[7] For routine-control work, filter paper is sometimes more convenient than a prepared Gooch crucible. It must be very carefully washed to remove the last traces of fat, especially the rim.

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the kerosene burns quietly. Ash the residue in a muffle, to constant weight, taking care that the decomposition of carbonates is complete, and report the result as soluble mineral matter.[8]

Free Fatty Acids.

The ALCOHOL[9] used shall be approximately 95 per cent. ethyl alcohol, freshly distilled from sodium hydroxide, which with phenolphthalein gives a definite and distinct end-point.

DETERMINATION.—Weigh 1 to 15 grams of the prepared sample into an Erlenmeyer flask, using the smaller quantity in the case of dark colored, high acid fats. Add 50 to 100 cc. hot, neutral alcohol, and titrate with N/2, N/4 or N/10 sodium hydroxide, depending on the fatty acid content, using phenolphthalein as indicator. Calculate to oleic acid. In the case of palm oil the results may also be expressed in terms of palmitic acid, clearly indicating the two methods of calculation in the report.

Titer.

STANDARD THERMOMETER.—The thermometer is graduated at zero and in tenths of a degree from 10 to 65°, with one auxiliary reservoir at the upper end and another between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark is at least 1 centimeter below the 10° mark; the 10° mark is about 3 or 4 centimeters above the bulb, the length of the thermometer being about 37 centimeters over all. The thermometer has been annealed for 75 hours at 450° C. and the bulb is of Jena normal 16''' glass, or its equivalent, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 centimeters long and 6 millimeters in diameter. The stem of the thermometer is 6 millimeters in diameter and made of the best thermometer tubing, with scale

[8] For routine work, an ash may be run on the original fat, and the soluble mineral matter obtained by deducting the ash on the insoluble impurities from this. In this case the Gooch crucible should be prepared with an ignited asbestos mat so that the impurities may be ashed directly after being weighed. In all cases ignition should be to constant weight so as to insure complete decomposition of carbonates.

[9] For routine work methyl or denatured ethyl alcohol of approximately 95 per cent. strength may be used. With these reagents the end point is not sharp.

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etched on the stem; the graduation is clear cut and distinct, but quite fine. The thermometer must be certified by the U. S. Bureau of Standards.

GLYCEROL CAUSTIC SOLUTION.—Dissolve 250 grams potassium hydroxide in 1000 cc. dynamite glycerin with the aid of heat.

DETERMINATION.[10]—Heat 75 cc. of the gycerol-caustic solution to 150° C. and add 50 grams of the melted fat. Stir the mixture well and continue heating until the melt is homogeneous, at no time allowing the temperature to exceed 150° C. Allow to cool somewhat and carefully add 50 cc. of 30 per cent. sulfuric acid. Now add hot water and heat until the fatty acids separate out perfectly clear. Draw off the acid water and wash the fatty acids with hot water until free from mineral acid, then filter and heat to 130° C. as rapidly as possible, with stirring. Transfer the fatty acids, when cooled somewhat, to a 1 inch by 4 inch titer tube, placed in a 16-ounce salt-mouth bottle of clear glass, fitted with a cork which is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 revolutions per minute) until the mercury remains stationary for 30 seconds. Allow the thermometer to hang quietly with the bulb in the center of the tube and report the highest point to which the mercury rises as the titer of the fatty acids. The titer should be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

Unsaponifiable Matter.

EXTRACTION CYLINDER.—The cylinder shall be glass stoppered, graduated at 40 cc., 80 cc. and 130 cc. and of the following dimensions; diameter about 1⅜ inches, height about 12 inches.

PETROLEUM ETHER.—Redistilled petroleum ether boiling under 75° C. shall be used. A blank must be made by evaporating 250 cc. with about 0.25 gram of stearin or other hard fat (previously brought to constant weight by heating) and drying as in the actual determination. The blank must not exceed a few milligrams.

DETERMINATION.—Weigh 5 grams (±0.20 gram) of the prepared sample into a 200 cc. Erlenmeyer flask, add 30 cc. of re-

[10] For routine work during period of high prices see p. 24.

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distilled 95 per cent. (approximately) ethyl alcohol and 5 cc. of 50 per cent. aqueous potassium hydroxide, and boil the mixture for 1 hour under a reflux condenser. Transfer to the extraction cylinder and wash to the 40 cc. mark with redistilled 95 per cent. ethyl alcohol. Complete the transfer, first with warm, then with cold water, till the total volume amounts to 80 cc. Cool the cylinder and contents to room temperature and add 50 cc. of petroleum ether. Shake vigorously for 1 minute and allow to settle until both layers are clear, when the volume of the upper layer should be about 40 cc. Draw off the petroleum ether layer as closely as possible by means of a slender glass siphon into a separately funnel of 500 cc. capacity. Repeat extraction four more times, using 50 cc. of petroleum ether each time.[11]

Wash the combined extracts in a separatory funnel three times with 25-cc. portions of 10 per cent. alcohol, shaking vigorously each time. Transfer the petroleum ether extract to a wide-mouth tared flask or beaker, and evaporate the petroleum ether on a steam bath in an air current. Dry as in the method for moisture and volatile matter. Any blank must be deducted from this weight before calculating unsaponifiable matter. Test the final residue for solubility in 50 cc. petroleum ether at room temperature. Filter and wash free from the insoluble residue, if any, evaporate and dry in the same manner as before.

NOTES ON THE ABOVE TENTATIVE METHODS.

Sampling.

The standard size sample adopted by the Committee is at least 3 pounds in weight. The Committee realizes that this amount is larger than any samples furnished representing shipments of from 20,000 to 60,000 pounds, but it believes that the requirement of a larger sample is desirable and will work toward uniform and more concordant results in analysis. It will probably continue to be the custom of the trade to submit smaller buyers' samples than required by the Committee, but these are to be considered only as samples for inspection and not for analysis. The standard analytical sample must consist of 3 pounds or more.

The reasons for keeping samples in a dark, cool place are ob-

[11] When the unsaponifiable matter runs over 5 per cent., more extractions are recommended.

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vious. This is to prevent an increase in rancidity and any undue increase in fatty acids. In the case of many fats the Committee has found in its co-operative analytical work that free acid tends to increase very rapidly. This tendency is minimized by low temperatures.

Moisture and Volatile Matter.

After careful consideration the Committee has decided that moisture is best determined in a vacuum oven of the design which accompanied the above report. Numerous results on check samples have confirmed the Committee's conclusions. The oven recommended by the Committee is constructed on the basis of well-known principles and it is hoped that this type will be adopted generally by chemists who are called upon to analyze fats and oils. The experiments of the Committee indicate that it is a most difficult matter to design a vacuum oven which will produce uniform temperature throughout, and one of the principal ideas in the design adopted is uniformity of temperature over the entire single shelf. This idea has not quite been realized in practice, but, nevertheless, the present design approaches much closer to the ideal than other vacuum ovens commonly used. In the drawing shown the essential dimensions are those between the heating units and the shelf and the length and breadth of the outer casting. The standard Fat Analysis Committee oven (F. A. C. oven) can be furnished by Messrs. E. H. Sargent & Co., 125 West Lake Street, Chicago, Ill.

The Committee realizes that for routine work a quicker method is desirable and has added one such method and has also stated the conditions under which comparable results can be obtained by means of the ordinary well ventilated air oven held at 105 to 110° C. However, in accordance with a fundamental principle adopted by the Committee at its first meeting, only one standard method is adopted and declared official for each determination.

The Committee realizes that in the case of all methods for determining moisture by means of loss on heating that there may be a loss due to volatile matter (especially fatty acids) other than water. The title of the determination moisture and volatile matter indicates this idea, but any considerable error from this source may occur only in the case of high acid fats and oils and

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particularly those containing lower fatty acids such as coconut and palm kernel oil, work on which is now in progress to be reported at a later date. In the case of extracted greases which have not been properly purified, some of the solvent may also be included in the moisture and volatile matter determination but inasmuch as the solvent, usually a petroleum product, can be considered only as foreign matter, for commercial purposes it is entirely proper to include it with the moisture. The Committee has also considered the various distillation methods for the determination of moisture in fats and oils, but since, according to the fundamental principles which it was endeavoring to follow, it could standardize only one method, it was decided that the most desirable one on the whole was the vacuum oven method as given. There are cases wherein a chemist may find it desirable to check a moisture determination or investigate the moisture content of a fat or oil further by means of one of the distillation methods.

Insoluble Impurities.

This determination, the title for which was adopted after careful consideration, determines the impurities which have generally been known as dirt, suspended matter, suspended solids, foreign solids, foreign matter, etc., in the past. The first solvent recommended by the committee is hot kerosene to be followed by petroleum ether kept at ordinary room temperature. Petroleum ether, cold or only slightly warm, is not a good fat and metallic soap solvent, whereas hot kerosene dissolves these substances readily, and for this reason the Committee has recommended the double solvent method so as to exclude metallic soaps which are determined below as soluble mineral matter.

Soluble Mineral Matter.

Soluble mineral matter represents mineral matter combined with fatty acids in the form of soaps in solution in the fat or oil. Formerly, this mineral matter was often determined in combination by weighing the separated metallic soap or by weighing it in conjunction with the insoluble impurities. Since the soaps present consist mostly of lime soap, it has been customary to calculate the lime present therein by taking one-tenth the weight of the total metallic soaps. The standard method as given above

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is direct and involves no calculation. The routine method given in the note has been placed among the methods, although not adopted as a standard method, for the reason that it is in use in some laboratories regularly. It should be pointed out, however, that the method cannot be considered accurate for the reason that insoluble impurities may vary from sample to sample to a considerable extent and the error due to the presence of large particles of insoluble impurities is thus transferred to the soluble mineral matter.

Free Fatty Acid.

The fatty acid method adopted is sufficiently accurate for commercial purposes. In many routine laboratories the fat or oil is measured and not weighed but the Committee recommends weighing the sample in all cases. For scientific purposes the result is often expressed as "acid number," meaning the number of milligrams of KOH required to neutralize the free acids in 1 gram of fat, but the commercial practice has been, and is, to express the fatty acid as oleic acid or, in the case of palm oil, as palmitic acid, in some instances. The Committee sees no objection to the continuation of this custom so long as the analytical report clearly indicates how the free acid is expressed. For a more exact expression of the free acid in a given fat, the Committee recommends that the ratio of acid number to saponification number be used. This method of expressing results is subject to error when unsaponifiable fatty matter is present since the result expresses the ratio of free fatty acid to total saponifiable fatty matter present.

Titer.

At the present time the prices of glycerol and caustic potash are abnormally high but the Committee has considered that the methods adopted are for normal times and normal prices. For routine work during the period of high prices the following method may be used for preparing the fatty acids and is recommended by the Committee:

Fifty grams of fat are saponified with 60 cc. of a solution of two parts of methyl alcohol to one of 50 per cent. NaOH. The soap is dried, pulverized and dissolved in 1000 cc. of water in a porcelain dish and then decomposed with 25 cc. of 75 per cent.

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sulfuric acid. The fatty acids are boiled until clear oil is formed and then collected and settled in a 150-cc. beaker and filtered into a 50-cc. beaker. They are then heated to 130° C. as rapidly as possible with stirring and transferred, after they have cooled somewhat, to the usual 1 inch by 4 inches titer tube.

The method of taking the titer, including handling the thermometer, to be followed is the same as that described in the standard method. Even at present high prices many laboratories are using the gycerol-caustic potash method for preparing the fatty acids, figuring that the saving of time more than compensates for the extra cost of the reagents.

Unsaponifiable Matter.

The Committee has considered unsaponifiable matter to include those substances frequently found dissolved in fats and oils which are not saponified by the caustic alkalies and which at the same time are soluble in the ordinary fat solvents. The term includes such substances as the higher alcohols, such as cholesterol which is found in animal fats, phytosterol found in some vegetable fats, paraffin and petroleum oils, etc. Unsaponifiable matter should not be confused in the lay mind with insoluble impurities or soluble mineral matter. The method adopted by the Committee has been selected only after the most careful consideration of other methods such as the dry extraction method and the wet method making use of the separatory funnel. At first consideration the dry extraction process would seem to offer the best basis for an unsaponifiable matter method, but in practice it has been found absolutely impossible for different analysts to obtain agreeing results when using any of the dry extraction methods proposed. Therefore, this method had to be abandoned after numerous trials, although several members of the Committee strongly favored it in the beginning. Again, at first glance, it would seem that the use of a siphon instead of a separatory funnel would be undesirable, but as a matter of fact in practice it is found to be more satisfactory than the separatory funnel, as well as much cheaper.

In carrying out the unsaponifiable determination in a routine way, the Committee has found that the ordinary 250-cc. graduated and stoppered cylinder is reasonably satisfactory for the purpose.

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One member of the Committee, Mr. Ernst Twitchell of the Emery Candle Company, Cincinnati, Ohio, was an earnest advocate of another method devised by him for the determination of unsaponifiable matter as opposed to the method finally adopted by the Committee. Mr. Twitchell's method is published in this *Journal*, 7 (1915), 217, under the title, "Unsaponifiable Matter in Greases."

In brief, the Twitchell method consists in saponifying with alcoholic potash and evaporating to dryness. The soap is then dissolved in water containing 20 per cent. alcohol approximately, and shaken out with ether in a separatory funnel. The combined ether extracts are shaken with dilute hydrochloric acid, washed with water, transferred to a weighed dish, evaporated, dried and weighed. The residue consists of unsaponifiable matter and fatty acids since the ether dissolves some soap which is afterward decomposed by the hydrochloric acid. The weighed residue is taken up with neutral alcohol and the fatty acids therein determined by titration with standard alkali solution. The fatty acids thus determined are calculated as oleic and deducted from the weight before obtained.

Under date of April 17, 1916, Mr. Twitchell wrote to the committee on the subject of his method which he recommended, as follows:

"At the last meeting I was requested to give in writing my arguments in favor of my method of determining unsaponifiable matter as published in *The Journal of Industrial and Engineering Chemistry*, March, 1915 (reprint enclosed herewith). I don't want to advocate this particular method or urge its adoption by the Committee, but I do want to say that I consider that the work of the Committee has proved that petroleum ether is not a suitable solvent for the extraction of unsaponifiable matter, for with one of the few samples examined (the yellow grease) the results obtained by, I believe, all the members of the Committee, show that ether extracts from 25 to 30 per cent. more than petroleum ether. Although with the other samples the two solvents gave about the same results, yet the fact that the petroleum ether failed with one should condemn it for all. I don't see how we can get away from this conclusion. I enclose a table of figures for unsaponifiable in the yellow grease, made with ether and with petroleum ether. I understand besides that the results obtained with ether by other members of the Committee were nearly the same as mine.

"I should be obliged to you if, when turning over the proceedings of the Committee to the new one which is to be formed, you would include

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what I have said above regarding *saponification* and *unsaponifiable* as a minority report.

"At the last meeting my method of determining unsaponifiable was criticised because of the varying corrections for soap in the ether. I hardly look at the determination of fatty acids as a correction, it being so easily, quickly and accurately made. It might almost be considered as the principal operation, and the washing out of the soap solution as a removal of the *bulk* of the fatty acids after which the remainder can be accurately titrated."

Mr. Twitchell's statements about a certain sample of yellow grease with which the Committee experienced some difficulty are correct, but it was found afterward that this sample was abnormal in that it contained some wool grease or lanolin, and it is a question whether or not even Mr. Twitchell's results were high enough in consideration of this fact. In short, this sample was considered by the Committee so abnormal that results were not to be trusted and other samples were substituted for further co-operative work.

The Committee, following its rule of adopting only one standard method, has to choose between Mr. Twitchell's method and the method finally adopted. One of the principal arguments against Mr. Twitchell's method is the correction for the fatty acids. This correction is variable and in many cases amounts to several times the amount of unsaponifiable matter determined, being usually from 0.5 to 2.5 times the amount of unsaponifiable matter in the hands of the average analyst. The Committee did not feel that it could consistently adopt a method involving so large a correction, even though the final results were generally good.

The old argument in regard to ethyl ether *vs.* petroleum ether as a solvent for unsaponifiable was carefully considered by the Committee. It is freely admitted that ethyl ether is a better solvent than petroleum ether, but in the opinion of the Committee it is too universal a solvent for the purpose inasmuch as it absorbs soap from a water solution. On the other hand, petroleum ether is selective in its action and shows little or no tendency to dissolve soaps. Again, commercial ethyl ether is an impure product containing in solution both water and alcohol as well as organic impurities of various sorts including peroxides. It has been recommended chiefly perhaps for two reasons: (1) it is a chemical of definite composition, and (2) it is a very general

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solvent for unsaponifiable substances. Petroleum ether has been criticised because it is not of constant composition or boiling point. It consists of various hydrocarbons of various boiling points and varies again depending on the source of the crude petroleum from which it was distilled. The Committee considered that its great recommendations were its selective solvent power, its immiscibility with water, its stability as regards decomposition on standing and its cheapness. Although it may vary slightly in solvent power when derived from different sources, even under the boiling point (75° C.) recommended by the Committee, nevertheless, all samples have sufficient solvent power for the determination in question if the Committee's directions are followed.

Taking everything into consideration, the Committee decided in favor of petroleum ether as the solvent and finally adopted the method specified above, and it is believed that this method will be found quite satisfactory for the purpose.

NOTES ON CHROME LIQUORS.*

By J. R. Blockey, M. Sc.

The methods of chrome tanning may be roughly divided into two groups (*a*) processes involving one bath, and (*b*) processes involving two baths. This applies only to the actual tanning processes and not to the many processes incidental to the tanning, such as deliming, pickling or neutralizing.

In the one-bath process the goods are tanned in one liquor and the tannage is gradual and progressive. As an example the use of chrome alum made basic by means of soda may be taken. In such a case the goods are immersed in the basic chrome liquor and the tannage proceeds from the outsides to the insides in a similar manner to ordinary vegetable tannage.

In the two-bath process the changes are quite different. Take for example the common method using bichromate of soda (or of potash) and hydrochloric acid for the first bath, and hyposulphite of soda for the second bath. In this case the goods are first impregnated with chromic acid (which has no tanning action) and are then immersed in hyposulphite of soda solution (which has no tanning action), but which reduced the chromic

* *S. & L. Reporter.*

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acid to such a form that it is capable of tanning the fiber. This then is briefly the main difference between the one-bath and the two-bath processes, that in the former the tannage is progressive like vegetable tannage, and in the latter the tanning agent is produced actually on the fiber so that the tannage is sudden. This outline will serve as an introduction to the question of the differences in the leather produced by the two processes, and to the question of the relative advantages of the two processes.

The most common plan of carrying out the one-bath process is to buy the liquors ready made. This plan possesses the advantage of being easy and of ensuring uniformity of liquor. The makers who specialize in these one-bath liquors can be relied upon to maintain absolute uniformity of composition with different deliveries. They also are in a position to modify the character of the liquor to suit different purposes. (Just as different vegetable tanning materials produce different tannages, and are therefore used in the production of different classes of leather, so modifications of the composition of the chrome liquor will produce different tannages also suitable for different classes of leather.)

These ready made bought chrome liquors are all made from chromium in what is called the trivalent condition. The commonest example is chrome alum made basic by means of soda. Chrome alum is a double salt of chromium sulphate and potassium sulphate, the latter of which plays no part in the actual chrome tanning. The chromium sulphate is the actual tanning agent. Its chemical formula is $Cr_2(SO_4)_3$. Chromium chloride is also the basis of many of these one-bath chrome liquors and its formula is $CrCl_3$. In both these salts the chromium is a trivalent form. In the trivalent form 1 atom of chromium is combined with 3 atoms of a monovalent element such as chlorine, *e. g.* $CrCl_3$ or 2 atoms of chromium are combined with 3 atoms of a divalent element or group of elements, *e. g.* Cr_2O_3 and in fact, it is only in the trivalent form that chromium salts can produce leather. In bichromate of soda or of potash, the chromium is in a hexavalent form and it must be changed to the trivalent form before it can be made to convert hide fiber into leather. This difference is the basis or cause of most of the differences between one-bath and two-bath tannages.

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The simplest form of one-bath liquor is that made from chrome alum. In solution chrome alum dissociates so that the solution is acid, and although this solution is made basic by the addition of soda, it is still acid as determined by litmus and other tests. This appears rather like a contradiction in terms, that a basic solution can be acid in reaction, but even the most basic chrome liquor must be acid in order that tanning may occur. The confusion disappears when it is pointed out that the terms basic and alkaline are not synonymous.

When chromium chloride (which may be taken for illustration instead of chromium sulphate or chrome alum, as being simpler) is dissolved in water, it behaves as though it split up into free hydrochloric acid and a different salt of chromium. The change may be represented thus:

$$Cr_2Cl_6 + H_2O = Cr_2(OH)Cl_5 + HCl$$

The addition of soda to such a solution neutralizes the free acid and leaves a salt of chromium containing less than the original chromium salt.

The free hydrochloric acid in the above equation is neutralized by the soda, and the salt $Cr_2(OH)Cl_5$ is left. On adding more soda the hydrolysis proceeds further until the final stage of $Cr_2(OH)_6$ is reached which is insoluble and is precipitated. A salt such as Cr_2Cl_6 in which the whole of the base is combined with acid is called a normal salt, while a basic salt is intermediate between the normal salt and the base or hydrated oxide. Thus Cr_2OHCl_5 is a basic salt. The possible salts ranging from normal chromium chloride to chromium hydrate are Cr_2Cl_6; $Cr_2(OH)Cl_5$; $Cr_2(OH)_2Cl_4$ or $Cr(OH)Cl_2$; $Cr_2(OH)_3Cl_3$; $Cr_2(OH)_4Cl_2$ or $Cr(OH)_2Cl$; $Cr_2(OH)_5Cl$; $Cr_2(OH)_6$ or $Cr(OH)_3$. It will be seen that each stage represents the replacement of 1 atom of Cl by OH. The normal salt will penetrate pelt rapidly and evenly but the tannage is empty and poor. The more basic the salt the slower will the tanning effect penetrate and the heavier will be the final tannage. The variation in the basicity of the salt has the greatest influence on the character of the leather.

With chromium sulphate or chrome alum the salts are as follows, ranging from the normal salt to the complete base: $Cr_2(SO_4)_3$; $Cr_2(OH)_2(SO_4)_2$ or $Cr(OH)SO_4$, $Cr_2(OH)_4SO_4$

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and $Cr_2(OH)_6$. The same influence of increasing basicity is present as with the chloride. The second salt $Cr_2(OH)_2(SO_4)_2$ or $Cr(OH)SO_4$ is often regarded as the most suitable for general purposes. Such a salt is obtained by adding washing soda to chrome alum in the proportion of 1 molecule to 1 molecule, that is, 286 parts of soda crystals to 998 parts of chrome alum. In practice the production varies from 2½ to 3½ parts of soda crystals to 10 parts of chrome alum.

Such a basic salt can be made, in addition to the way just outlined, by dissolving chromium hydroxide in sulphuric acid, and also by reducing bichromate of soda or potash.

In bichromate the chromium is not in the trivalent form and before it can be made to tan, it must be brought to this form. The formula for potassium bichromate is $K_2Cr_2O_7$ which can also be written thus K_2O,Cr_2O_6 showing that 2 atoms of chromium are combined with 6 atoms of oxygen. In order to make the chromium correspond to the condition suitable for tanning, it is necessary to reduce the compound to such a state that only 3 atoms of oxygen are combined with 2 atoms of chromium. This can be achieved by removing oxygen from the bichromate. Organic substances such as glucose, cane sugar, and inorganic substances such as sodium bisulphite, are capable of reducing bichromate by removing oxygen. One molecule of bichromate can furnish 3 atoms of oxygen available for oxidizing either of these three substances.

$$Cr_2O_6 = Cr_2O_3 + 3O$$

The bichromate is reduced by means of the reducing agent, while the reducing agent (*i. e.* the glucose, etc.) is oxidized by the bichromate.

The products of the reaction are various, depending upon the reducing agent. On the one hand the chromium of the bichromate is reduced from the hexavalent form Cr_2O_6 to the trivalent form Cr_2O_3. The reduction is always carried out in the presence of sulphuric acid, which may be regarded, from the practical point of view, as being available to combine the Cr_2O_3 to form a basic chromium sulphate, such as is formed when chrome alum is made basic with soda. On the other hand the reducing agent is transformed into other substances, and it is the character and presence of these other substances which produce the variations in these

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reduced bichromate liquors, and which make these liquors different in character from the chrome alum—soda liquors. For instance, suppose cane sugar or glucose is used as reducing agent, the products of the oxidation of the cane sugar or glucose are complex. They vary with the proportions and the temperature of the reaction. More glucose or cane sugar than is absolutely necessary to produce complete reduction of the bichromate is almost always used, and therefore in such a liquor there will always be present free glucose or cane sugar, which almost certainly will have some effect on the tanning properties of the liquor. It is usually argued, for instance, that the excess of unaltered glucose or cane sugar helps to make a softer and fuller leather than would be the case if the theoretically required quantity were used. It is more probable that it is the decomposition products of the glucose which cause the difference between these reduced liquors and the liquors made by adding soda to chrome alum.

The glucose, in reducing the bichromate, is itself oxidized and the products of this oxidation are aldehydes and similar substances. Now aldehydes themselves have the property of converting hide fiber into leather. For instance, the Pullman Payne patent process for making buff leather was based on the use of formaldehyde itself, while in the process of making chamois leather by means of fish oils, the latter are, by atmospheric oxidation, converted into aldehydic bodies such as acrolein, which play a part in the conversion of the pelt into leather. Since aldehydic bodies are produced in the reduction of bichromate by means of glucose or other organic materials, it is not surprising that the tannage produced by these reduced bichromate liquors is different from that produced by the simpler chrome alum and soda liquors.

A word might be said here about those reduced bichromate liquors which are reduced by means of such inorganic substances as sodium bisulphite. These liquors are made in a similar manner to that described using glucose or cane sugar. The bichromate is acidified with sulphuric acid and the reducing agent, sodium sulphite or sodium bisulphite, is added gradually to the mixture until the whole of the bichromate has been reduced. This method has one or two advantages over the glucose method. In the

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first place the reduction will take place in the cold, so that there is no need to heat the mixture of bichromate and sulphuric acid as with glucose. Of course, the reaction between the bisulphite and the chromic acid liberates heat and the mixture soon reaches boiling point, but there is no need to heat the mixture beforehand to enable the reaction to take place. The other advantage over the use of glucose is that the result is more uniform. When using glucose there is a danger of various reactions setting in, for instance the color of the liquor may become greenish blue as it should do, or it may develop a violet shade, which is a sign of a wrong reaction. The violet shade is most likely to occur with impure varieties of glucose and is scarcely, if ever, produced when cane sugar is used, which accounts for the wider popularity of the latter despite its higher cost.

When using sodium bisulphite as a reducing agent, there is little chance of a side reaction taking place, so that the results are nearly always uniform. The real reducing agent, whether sodium sulphite or bisulphite is used may be regarded as sulphur dioxide, SO_2, which is oxidized to the higher form SO_3 and the corresponding salts the sulphates. The by-products in these chrome liquors are therefore only sulphates and similar substances which play no part in the tannage.

Such liquors resemble very closely the liquors made from chrome alum and soda and also those made by dissolving chromium hydrate or oxide in sulphuric acid. They differ very much from the liquors made by reducing bichromate by means of glucose.

There are other ways of preparing one-bath chrome liquors than the ones already described, but they are all modifications of the two types of method. The main variation is the nature of the reducing agent in the case of the reduced bichromate liquor, which may be, in addition to those already cited, glycerine or dextrine, which are organic, and almost any inorganic reducing agent. In the case of the unreduced liquors the main variation is in the acid combined with the chromium. It usually is sulphuric acid, but it is often hydrochloric acid, and may even be an organic acid such as formic, acetic or lactic acid. When the chromium salts of these latter acids are used, the basicity

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of the salt may be very much lower than with say chromium sulphate or chloride to produce a good tannage.

It would take too much space to describe the individual peculiarities of every single liquor, but the above may serve to show the differences between the main types of one-bath liquors.

A more important question than that of the difference between the various one-bath liquors, is that of the difference between the one-bath process and the two-bath process. Something of the fundamental difference was described in the introductory paragraph.

The rough outline of the two-bath process is as follows: The goods to be tanned are immersed in a bath of bichromate of soda or potash, usually acidified with sulphuric acid. The sulphuric acid and the bichromate together form chromic acid as already described. If acid is not added to the bichromate it is usually because the skins themselves have been pickled with sulphuric acid and salt and therefore carry into the bichromate bath sufficient sulphuric acid to liberate the chromic acid from the bichromate.

In all the variations of this first bath, the object is the same, *viz.*, the impregnation of the skins with chromic acid.

The second bath is always composed of some reducing agent which converts the chromic acid into the trivalent form. The most common material used in the second bath is "hypo" or sodium thiosulphate, to which is added sulphuric acid. The proportions are usually chosen so that one product of the reaction has approximately the composition represented by the formula $Cr(OH)SO_4$ which, as already pointed out, is a suitable tanning salt.

The tanning salt may therefore be the same in both the one-bath and the two-bath process, with the important difference, of course, that in the former case the tannage proceeds gradually from the outsides to the insides and in the latter case the tannage occurs more or less momentarily and "in situ." One important difference that arises from this is that of speed. In the one-bath process the tanning agent being basic is more or less colloidal, and therefore penetrates the pelt only slowly compared with a crystalloidal substance such as bichromate. (The more basic a one-bath liquor the more colloidal is the tanning substance, and

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also the slower does it penetrate the pelt. The liquor can be made so basic and so colloidal that not only will it refuse to tan properly, but it will also precipitate on boiling or even on diluting. On the other hand if the liquor be made only slightly basic or even not at all basic, such as is represented by chrome alum alone, the liquor penetrates very rapidly, but the tannage produced is not only very slight but also very easily washed out again.)

In the two-bath process the materials are not used in the basic or colloidal form, and they therefore, penetrate the skins much more rapidly than basic chrome salts. Thus bichromate of soda can be made to penetrate pelt in as many hours as it would take days for a basic chrome salt to penetrate. Similarly hypo will penetrate pelt rapidly, so that although there are two distinct processes in the two-bath method, compared with only one in the single bath method, yet the time occupied in carrying out the former is less than in the latter. Against the apparent advantage of greater speed in the two-bath process must be placed however, the increased number of times the goods are handled, so that what is saved in time may be lost in labor.

Another disadvantage of the two-bath process is its complexity. The number of different reactions which can occur in the reducing bath is great. The relative proportions of bichromate, acid and hypo (which may vary) influence the reactions which occur. This subject has been very thoroughly investigated by Stiasny and Das who traced very many possibilities. In the one-bath process however, having once made the liquor and determined the basicity, there is very little possibility of variation of tanning properties. It is therefore possible to maintain the tannage quite uniform not only in one lot of goods but also in successive lots. The one-bath process thus possesses the great virtues of simplicity and uniformity, which are particularly valuable where no elaborate chemical control is possible. It ought to be pointed out, however, that there is one case of one-bath tanning in which even or uniform tanning is not always obtained. If the liquor be made very basic, to such a point say, that it precipitates on diluting or warming, the tanning may be irregular. When pelt is placed in such a liquor the outsides immediately are heavily tanned, and the tannage may be so heavy that penetration becomes very slow and difficult. The action is in fact similar to that which would

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occur if pelt were placed in strong vegetable liquors which are very astringent. The outsides become overtanned while penetration becomes almost stopped. In the case of the basic chrome liquor, the liquor itself undergoes a change, with the result that the pelt, particularly if it is stout, becomes tanned on the outsides with a basic salt, while the liquor which penetrates is less basic. The visible result is a difference in color of the cut section.

If a cut section be made in a thick place, it would be found that the interior presented a light bluish cast, compared with the darker greenish color of the outsides.

One successful plan to obviate this is to commence the tannage in liquors not very basic and continue the tannage in liquors of gradually increasing basicity. The plan is somewhat analogous to the method employed in vegetable tanning to start in mellow liquors and complete in astringent liquors.

By starting in slightly basic liquors the tannage penetrates evenly but lightly, and by completing in more basic liquors the tannage is increased evenly throughout the section.

Perhaps the greatest difference between the one-bath and the two-bath processes is due to sulphur. It has been pointed out that the actual tanning agent may be the same in both cases, so that any difference should be sought for, more in side reactions than in the main reactions. One of these side reactions which occur in the two-bath process but not in the one-bath process is that between hypo and acid. Hypo is the commonest reducing agent employed, and is used along with acid, generally hydrochloric. The main function of the hypo is, of course, to reduce the chromic acid to a trivalent chromium salt, and most of the hypo is so used up, but a side reaction between the hypo and the acid always takes place, but to a varying extent, depending upon the relative proportions, concentrations and temperatures. In its simplest form the reaction may be represented thus:

$$\underset{\text{hypo}}{Na_2S_2O_3} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{2HCl} = \underset{\text{common salt}}{2NaCl} + \underset{\substack{\text{sulphur}\\\text{dioxide}}}{SO_2} + \underset{\substack{\text{free}\\\text{sulphur}}}{S}$$

Of the products of the reaction, common salt plays no part, the sulphur dioxide is the reducing agent for the chromic acid, while the sulphur is deposited in the free form. It is this sulphur which produces the turbidity when the acid is added to the hypo

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in making up the reducing liquor. The sulphur is partly deposited in the liquor, but also largely on the fibers of the leather, which produces the main difference between one-bath and two-bath tanned leather. The deposition of the sulphur on the grain of the leather helps to make it whiter than one-bath tanned leather. The deposition on the fibers helps to make the leather mellow and soft by acting as a sort of lubricant by allowing the fibers to slip over one another more readily.

It is usually held that it is this sulphur which causes the main difference between the two classes of leather: it is not to be wondered at therefore that attempts have been made to apply some process to one-bath tanned leather to deposit sulphur on the fibers and so make the leather approximate to two-bath tanned leather. Eitner has suggested a process which succeeds to some extent. The method consists in treating the goods either before or after tanning with alternate baths of hypo and acid. This enables the reaction represented by the above equation to take place so that free sulphur is deposited on the fiber.

Similarly Procter has suggested treating the leather in the wet chromed state and without washing out the excess of chrome liquor, with an excess of a solution of hypo or of an alkaline polysulphide which will liberate free sulphur on the fibers.

The whole question of sulphur only arises when hypo or a similar substance is used in the reducing bath. Other substances have been recommended for this purpose from which no sulphur can be deposited. For instance, bisulphite of soda is now very widely used in place of hypo. In this case the reducing agent is sulphur dioxide and no sulphur is deposited.

Leather tanned in this way is more similar to one-bath tanned leather than when hypo is used.

Since the reduction in the two-bath process takes place in contact with the pelt, it follows that the reducing agent must be able to work in the cold, because a high temperature would be out of the question. The organic reducing agents such as glucose, cane sugar, glycerine, which can be used in making a one-bath liquor, cannot be used for reducing in the two-bath process, because they will only reduce the bichromate or chromic acid at a temperature higher than that which pelt will withstand.

It will be seen from the foregoing that the one-bath process is

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not only more simple than the two-bath process, but is more uniform in its results and is capable of such modifications that it is possible to produce most of the effects of the latter process, and it is not surprising therefore that the two-bath process is gradually being ousted by the one-bath process.

ABSTRACTS.

The Chemical Composition of Lime-sulphur Animal Dips.—ROBERT M. CHAPIN. U. S. Dept. of Agri., *Bulletin No.* 451. The reactions which determine the composition of lime-sulphur solutions made by boiling lime and sulphur in water are numerous. Some of them are reversible, the points of equilibrium varying with temperature, with concentration and also with other conditions. The effect of varied conditions of preparation upon the resulting solutions was noted. Thus, the ratio of lime to sulphur, the amount of water used for boiling and the time of boiling were all varied and the solutions analized. A general idea of their composition may be obtained from the following example: A liquor was made by boiling 45 parts CaO, 100 parts S and 515 parts water under a reflux condenser for 1 hour; cooled in an atmosphere of coal gas (which had been passed through sodium hydrate) and then stored in a tightly corked bottle for 2 months. The clear liquor contained (in grams per 100 cc.) 3.26 per cent. S as thiosulphate, 0.05 per cent. S as hydrogen sulphide, 3.04 per cent. S as monosulphur and 11.67 per cent. S as polysulphur. The value found X in the M_2Sx present, is 4.84, or roughly 5, and the molecular ratio of M_2Sx to $M_2S_2O_3$ is 1.86, or about 2.

For the estimation of available lime in the sample used for these experiments, the author found the method of Lindet and Brasart to be convenient. (Abstr. *Journ. Soc. Chem. Ind.* 1910. Vol. 29, p. 643.) The available lime is dissolved in phenol and the solution titrated with standard hydrochloric acid. D. Mc. C.

Some New Methods for the Analysis of Lime Sulphur Solutions.—ROBERT M. CHAPIN. *Journal Ind. & Eng. Chem.*, 1916, Vol. 8, p. 151. The article deals with the analysis of solutions used for dipping cattle and sheep. The solutions are made by boiling various proportions of lime and sulphur in water and usually contain from 1.5 per cent. to 2.0 per cent. of sulphur as sulphide. The ordinary method of determining the alkalinity of such liquors consists of titrating the clear settled solution with standard hydrochloric acid until the characteristic yellow color has gone, adding metlyl orange or congo red and completing the titration to a definite end point. Addition of the indicator is delayed as long as possible, as the color is rapidly bleached or absorbed by freshly precipitated sulphur. This method fails when applied to liquors which have been frequently used for dipping, on account of the interference of the dissolved organic matter. The writer suggests the use of sodium nitroprusside as external

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indicator in such cases, taking advantage of the fact that this compound, in the presence of hydrogen sulphide only develops a violet color in alkaline solution. As the neutral point is approached, the violet color produced by the titrated liquor and the indicator becomes very faint. The end point is finally shown by the failure of a dirty green turbidity (in no way resembling the original violet) to appear within 15 minutes of quiet standing in diffused daylight. No claim is made as to the utility of the method for any other purpose than the titration of lime sulphur solutions and it is pointed out that it does not give satisfactory results with aqueous sodium sulphide solutions.

Soluble sulphides are determined by an interesting method based upon the reaction represented by the equation: $M_2Sx + M_2S_4O_6 = 2\,M_2S_2O_3 + xS$. The sulphide solution is made alkaline with ammonia and titrated with N/20 sodium tetrathionate using either nickel sulphate or sodium nitroprusside as external indicator, until no trace of sulphide remains. At the end point, nickel sulphate shows a color changing from faint gray to bluish green, the end point being much sharper than can be obtained when a metallic salt solution is used as titrating agent. When a very dirty lime-sulphur solution is dealt with, sodium nitroprusside is preferred as indicator. Using the former indicator a correction of 0.2 cc. is added to the titration; with the latter 0.4 cc. is added. The addition of varying amounts of sodium hydrate and ammonia to a given lime-sulphur liquor produced no appreciable effect on the titration results.

A N/20 sodium tetrathionate solution is prepared by adding N/10 sodium thiosulphate to N/10 iodine until the yellow color is just discharged, the final portion of thiosulphate being added from a burette. As sodium tetrathionate decomposes slowly in solution it should be prepared shortly before using. D. Mc. C.

The Indian Tanning Industry.—*Jour. Royal Society of Arts,* Nov. 9, 1917. Speaking in the Imperial Legislative Council on September 5th, the Viceroy, Lord Chelmsford, said that in order to meet the war office demand for leather tanners in India, orders have now been given on a scale that has encouraged them to reform their methods, and by having to work regularly to a rigid standard of high quality a striking improvement has already taken place. The Munitions Board, with the generous consent of a group of Central Indian States, has taken over the tannery at Maihar to test new tan stuffs, new combinations of known materials, new processes, and the manufacture of concentrated tan extracts. Those results which on an experimental scale appear to be successful are being tested on a commercial scale at the Allahabad tannery, recently purchased for the purpose. The results, as they become established, will be published for the benefit of tanners in other parts of India. A certain number of students are already being entertained as apprentices, and it is hoped later on to develop this side of the work by the formation at Allahabad of an institute in which the scientific aspects of tanning will be taught in conjunction with practical work on a commercial scale in the tannery itself.

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Paper from Spent Bark.—*Journal Royal Society of Arts,* Nov. 9, 1917. The *Leather World* draws attention to a new use of spent wattle bark. It appears that the Imperial Institute authorities are highly satisfied with the result of tests, undertaken in the Institute laboratories, concerning the suitability of Natal wattle bark (after it has been discarded by the tanners) for the manufacture of paper. These tests, which were on a small scale, demonstrated that a good quality brown paper can be manufactured from the spent bark. This paper bleaches readily to a cream tint, and has been pronounced eminently suitable for newspaper purposes, and, with further treatment, may make serviceable writing paper. The Institute authorities have interested several large paper mills in these discoveries, and large-scale tests are now proceeding to confirm the experiments on a commercial basis.

Tanners Seek Hides of Sharks and Porpoises.—*Commerce Reports.* As a result of the policy adopted by the United States Bureau of Fisheries of furnishing the skins of sharks and other fishes to persons who wish to experiment with these products, more than 40 tanners have had an opportunity to give them a trial, and several companies are now in the market for the raw hides of sharks and porpoises.

The bureau recently revised its circular on the subject of skinning sharks and curing and boxing the skins for shipment, and has added illustrations showing where the cuts should be made in taking off the skin and giving an outline of a skin properly taken off. This information, together with the statement that tanners desire to obtain the raw materials, is being communicated to fishermen, and the latter are being urged to furnish the tanners with supplies. The names of tanners and the prices they are willing to pay are included in the circular.

Some cabinet makers in this country still use the skins of certain sharks for polishing purposes. The skins that heretofore have been used are those of one of the European sharks. The Bureau of Fisheries is now determining whether the skins of some of the sharks on our own coasts are not equally well suited for this purpose.

Comparative Tests in Chemical Glassware.[1]—*Jour. Ind. & Eng. Chem.,* Dec. 1917. The cutting off of imports from Germany and Austria has forced us to rely upon American manufacturers for practically our entire supply of glass beakers and flasks. In order to give chemists some information as to the quality of this ware, the Bureau of Standards has examined five brands of American-made ware in comparison with the two best known wares of European make.

The tests included chemical analysis, determination of coefficient of expansion, refractive index, condition of strain, resistance to repeated evaporation, to heat, and to mechanical shock, and resistance to chemical reagents.

In all cases beakers and flasks approximating in size the 400-cc. Jena

[1] Published by permission of the Director of the Bureau of Standards. An abridgement of a longer and more complete publication to be issued by the Bureau of Standards.

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beaker and flask were used. All the ware tested bore permanent trade marks. From 45 to 50 beakers and flasks of each ware were secured for this series of tests.

Table I gives the composition of the different wares tested.

Details regarding the methods of analysis, weight and size of pieces tested, coefficient of expansion, refractive indices, and condition of strain will appear in a publication of the Bureau of Standards and are not given here, since little information bearing on the suitability of the various glasses for laboratory use can be obtained from these results. The Pyrex ware has low coefficient of expansion and refractive index.

The evaporation test, which was made only on beakers, consisted in repeated evaporation to dryness of sodium chloride solution with examination for cracks after each evaporation. None of the wares developed cracks after twelve evaporations.

One of the heat shock tests consisted in filling the beakers with cold water, which was then rapidly heated to boiling. Other tests included the plunging into ice water of vessels containing boiling water, paraffin at 150° C., and paraffin at 200° C., and the dropping of beakers bottom down upon a thick board from heights increased by intervals of 5 inches.

The solubility tests were made by determining the loss in weight of pieces of the wares upon treatment with water and various solutions commonly used in the laboratory. With water on beakers the action was continued about 72 hours, the water being heated about 24 hours; on flasks, the action was continued about 17 hours, keeping the water boiling during 5 hours; with mineral acids, solutions containing sodium chloride and sodium nitrate were mixed with a large excess of sulfuric acid, boiled and heated for an hour after fumes of SO_3 appeared. With sodium and potassium carbonates and hydroxides and sodium phosphate half-normal solutions were boiled for 20 minutes in the vessels and in the case of beakers fresh half-normal solutions were subsequently evaporated in the same beakers. With ammonia, strong ammonia was allowed to stand 24 hours in the vessel, then diluted and boiled for 30 minutes. With ammonium sulfide and chloride, mixtures of twice normal salts were allowed to stand in the vessels 24 hours, then boiled for 30 minutes.

Table II shows the results of heat and mechanical shock tests. Figs. I to IV show the effects of the various reagents on the wares tested. In these figures individual accepted determinations are shown by dots, determinations which are believed to be in error and therefore omitted from the averages by circles. The lengths of the rectangles indicate the averages of accepted values. The letters *K, M, P, J, N, F,* and *L* indicate Kavalier, M. E. G. Co., Pyrex, Jena, Nonsol, Fry, and Libbey, respectively.

Table III gives a general summary of the resistance to the various solutions and to mechanical and heat shock of the wares tested. In this table the numerical exponents indicate the minor differences in resistance, the lowest number being the most resistant. The absence of an exponent indicates that the differences in resistances are too small to justify any differentiation between the wares graded in the same group. In the rating

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TABLE I.—ANALYSES.

Ware	Kavalier beaker	M. E. G. Co. beaker	Pyrex beaker	Jena beaker	Jena flask	Nonsol beaker	Fry beaker	Libbey beaker
Al_2O_3	0.14	1.0	2.0	4.2	4.2	2.5	2.7	2.1
Fe_2O_3	0.08	0.35	0.25	0.25	0.27	0.23	0.22	0.44
ZnO	....	5.6	....	10.9	10.9	7.8	3.6	....
PbO	....	....	....	....	....	....	....	1.0
MnO	0.02	0.02	0.01	0.01	0.01	0.01	0.03	0.03
CaO	8.7	0.66	0.29	0.63	0.56	0.79	2.6	0.42
MgO	0.17	4.3	0.06	0.21	0.25	3.4	2.6	0.08
Na_2O	7.1	10.8	4.4	7.5	7.8	10.9	9.8	8.2
K_2O	7.9	0.30	0.20	0.37	0.31	0.30	1.5	0.67
SiO_2	75.9	73.0	80.5	64.7	64.7	67.3	68.6	75.9
B_2O_3	....	3.6	11.8	10.9	10.6	6.2	8.1	10.8
P_2O_5	0.08	....	....	....	....	....	....	....
SO_3	0.20	0.02	....	....	....	....	....	....
As_2O_5	Trace	0.02	0.70	0.14	0.19	Trace	0.18	0.36
Sb_2O_5	....	0.60	....	....	....	0.62	....	....
TOTAL	100.29	100.27	100.21	99.81	99.79	100.05	99.93	100.00

Selenium and fluorine were not found, but lithium was detected spectroscopically by Mr. Paul W. Merrill in all the samples.

TABLE II.—HEAT AND MECHANICAL SHOCK TESTS.

No. refers to Number Tested. U, unaffected. F, failed. *b*, Broken. *c*, Cracked.

Ware	Water at 4° C. heated to boiling over direct flame: Beakers No.	U.	F.	Result	Flasks No.	U.	F.	Result	Boiled water and plunged into ice water: Beakers No.	U.	F.	Result	Flasks No.	U.	F.	Result	Paraffin heated in vessel to indicated temperature and vessel plunged into ice water: Heated to 150° C. Beakers No.	U.	F.	Result	Flasks No.	U.	F.	Result	Heated to 200° C. Beakers No.	U.	F.	Result	Flasks No.	U.	F.	Result	Drop Test-Beakers Only (6 of each ware tested) *No. that broke on Drop of:* 5 in.	10 in.	15 in.	20 in.	25 in.	30 in.	See *Note*
Kavalier	4	1	3*c*		0	..	..		2	2	0		0	..	..		2	1	1*c*		0	..	..		4	0	4*b*		0	..	..		4	2	..	..	..	..	...
M. E. G. Co.	2	2	0		4	2	2*c*		2	2	0		2	2	0		2	1	1*c*		4	3	1*c*		4	0	4*b*		2	0	2*b*		3	3	..	..	..	..	...
Pyrex	2	2	0		2	2	0		2	2	0		2	2	0		2	2	0		2	2	0		4	4	0		5	3	2*c*		..	..	1	..	1	1	(*m*)
Jena	2	2	0		2	2	0		2	2	0		2	2	0		2	2	0		2	2	0		4	1	3*b*		4	1	3*b*		2	3	..	1	..	..	...
Nonsol	2	2	0		2	2	0		2	2	0		2	2	0		2	2	0		2	2	0		4	4	0		4	0	4*b*		3	1	2	..	..	..	...
Fry	2	2	0		2	2	0		2	2	0		2	2	0		4	3	1*c*		4	3	1*c*		4	..	4*b*		4	0	4*b*		1	2	..	2	..	1	...
Libbey	2	2	0		2	2	0		2	2	0		2	2	0		4	4	0		4	4	..		4	4	0		4	0	4*b*		2	1	..	1	..	2	(*n*)

(*m*) One broke on bound at 25 in. and 2 did not break at 45 in. (*n*) One broke on bound at 20 in.

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of resistance to caustic alkalies the boiling tests only have been considered. These results indicate that all the American-made wares tested are superior to Kavalier and equal or superior to Jena ware for general chemical laboratory use.

TABLE III.—GENERAL SUMMARY OF TESTS.

Resistance to	Water	Mineral acids	Carbonated alkalies	Caustic alkalies	Ammonia and ammonium salts	Heat shock	Mechanical shock
Kavalier	Poor	Good	Poor	Good[2]	Good[2]	Poor	Poor
M. E. G. Co.	Good[3]	Good	Good[1]	Good[1]	Good	Poor	Poor
Pyrex	Good[2]	Good	Good[3]	Fair	Good	Good[1]	Good*
Jena	Good[4]	Good	Good[2]	Fair	Good	Good[3]	Pair
Nonsol	Good[3]	Good	Good[1]	Fair	Good	Good[2]	Fair
Fry	Good[4]	Good	Good[2]	Fair	Good	Poor	Good
Libbey	Good[1]	Good	Good[3]	Fair	Good	Good[2]	Good

* Far superior to any of the other wares

Ostrich Skin Leather.—*H. & L.*, November. The article shows a photograph and gives a description of bark-tanned ostrich skin. This leather was tanned by a firm in Scotland. In texture and thoughness it resembles pigskin leather. It is however marked with dark spots where the large feathers have been pulled. The average skin contains about 10 square feet that can be used and runs from 1 to 1½ millimeters in thickness. It can be used for fancy leather goods and for upper leather in shoes.

Vegetable Oil Industry in SaoPaulo, Brazil.—Consul C. L. HOOVER in *Commerce Reports*. This industry has largely developed as a result of the war.

The largest growth is in cotton seed oil. Large quantities of cotton are grown in this State and the seed which used to be wasted is now being worked up for oil. As a consequence the importations into the State have dropped from 2,000,000 pounds before the war to practically not any in 1917.

The demand for castor oil for use in aeroplane motors has stimulated the production of this oil. The castor bean grows wild and is so persistent that it was regarded as a pest. Consequently great quantities of this bean are available for oil making. Linseed oil and peanut oil are also now being made in small quantities. Peanuts grow wild in this State and there are almost unlimited supplies of these nuts available.

The forests of this State produce an immense variety of oil-bearing nuts. The cashew nut is perhaps the best known of these, but others are equally valuable for their oil. One, called the "unuba" nut, is 60 per cent. vegetable tallow; and another, called the "babasu," also contains 60 per cent. of oil. A babasu nut will burn for half an hour if a match is touched to it. Its kernel is much like copra and is excellent for soap making.

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THE CHEMICAL SERVICE SECTION OF THE NATIONAL ARMY.*

The importance of chemistry in the conduct of the war has received a gratifying endorsement from the war department in the establishment of a new division attached to the general staff and designated the Chemical Service Section of the National Army.

The two immediate purposes to be accomplished by the formation of this division are, *first,* the unification and more comprehensive development of the various research activities now being conducted for the war department, and *second,* the creation of a chemical organization, complete in personnel and equipment, for service with the American Expeditionary Forces in France.

The most significant feature in the formation of this section

* *J. I. E. C.*, Jan., 1918.

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is the growing appreciation on the part of the heads of the departments of the army of the value and necessity of chemistry in modern warfare. General Pershing has urgently requested that a chemical unit be organized and sent to France at the earliest possible moment to care for the emergency problems of vital importance which are constantly arising in the conduct of the war. Both the personnel and laboratory equipment of this force are being prepared upon the basis that the American armies in France have a right to the service of our ablest scientific minds and the most complete and adequate facilities for the work which it is possible for the United States Government to supply.

This chemical unit will serve as adviser to General Pershing on all chemical matters pertaining to the war, and will be attached to his staff through Colonel A. A. Fries, head of the Gas Warfare Division. It will also act as the chemical eyes of the unit in this country, transmitting information relative to chemical problems of the war to the men at work here. Able scientists throughout the country have responded eagerly to this call to national service. The unit will probably have sailed by the time this issue appears. The following have been recommended for commissions:

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About twenty-five enlisted men, including some of the best of the younger chemists of the country, make up the remaining personnel as at present organized. The names of these enlisted men are not yet available; they will be published in a future issue. As the work develops, more men will be added so that the laboratory will be in position to solve quickly the many problems which the constant changes in the methods and munitions of the war introduce.

In order that the information collected by this force of scientific men may be of the greatest aid to the research work now being conducted in this country, Dr. William H. Walker, of the Massachusetts Institute of Technology, has been commissioned a Lieutenant-Colonel, and will have charge of the unification and coordination of many lines of research now being so ably carried on here. It is not expedient to discuss the activities of these research groups, but it is gratifying to know that real progress is being made in practically every field.

The organization of this Chemical Service Section will provide a means by which men drafted into the service, and having special research ability, may be enabled to serve the country as scientists in a way which will produce results of the very highest value.

DISINFECTION REGULATIONS.

Special Order Prescribing Methods for the Disinfection of Hides, Skins, Fleshings, Hide Cuttings, Parings, and Glue Stock, and Other Animal By-products, Hay, Straw, Forage, or Similar Material Offered for Entry into the United States, and the Containers of Glue Stock, Bones, Hoofs, and Horns so Offered for Entry.

UNITED STATES DEPARTMENT OF AGRICULTURE,
Bureau of Animal Industry,

District of Columbia, December 14, 1917.

In accordance with the provisions of the United States Treasury Department and Department of Agriculture Joint Order No. 2 of October 15, 1917, "Regulations governing the sanitary handling and control of hides, fleshings, hide cuttings, parings, and glue stock, sheepskins and goatskins and parts thereof, hair, wool, and

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other animal by-products, hay, straw, forage, or similar material offered for entry into the United States," the following methods for the disinfection of the above-named materials and articles are hereby prescribed, effective January 1, 1918.

I. DISINFECTION OF HIDES AND SKINS PRIOR TO SHIPMENT.

Hides and skins disinfected prior to shipment as provided by regulation 1, Section 1, of said Joint Order No. 2, must be disinfected by one of the following methods:

(*a*) By immersion for not less than 24 hours in a 1 to 1,000 bichloride of mercury solution.

(*b*) By immersion for not less than 20 hours in a solution containing 2 per cent. absolute hydrochloric acid (hydrogen chloride) and 10 per cent. sodium chloride.

(*c*) By immersion for not less than 40 hours in a solution containing 1 per cent. absolute hydrochloric acid (hydrogen chloride) and 10 per cent. sodium chloride.

(*d*) By immersion for not less than 24 hours in a solution containing 1 per cent. formic acid, and mercuric chloride in the proportion of 1 part to 2,500 parts of the solution. Hides or skins treated by this process shall be held for 2 weeks following the treatment before neutralization.

(*e*) By dehairing and pickling in a solution of salt containing a definite percentage of mineral acid, and packing in barrels or casks while still wet with such solution, provided the hides or skins are not neutralized within 30 days after being so packed.

II. DISINFECTION OF HIDES AND SKINS AFTER ARRIVAL IN THE UNITED STATES.

Hides and skins required by regulation 1, Section 2, and regulation 2 of said Joint Order No. 2 to be disinfected on arrival at a United States port of entry shall be moved to an approved warehouse at such port or in sealed cars or containers to an establishment having proper facilities for their sanitary control and disinfection. They shall be stored and handled prior to disinfection in compartments set aside for that purpose, and all hides and skins stored or handled in such compartments shall be treated in accordance with the following rules:

1. All dust, litter, or waste arising from sorting, cutting, hand-

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ling, or moving said hides or skins prior to soaking, shall be burned or disinfected by exposure to a temperature of not less than 100° C. (212° F.) moist heat for not less than 15 minutes.

2. The hides and skins shall be subjected to disinfection by one of the following methods:

(*a*) By immersion for not less than 20 hours in a solution containing 2 per cent. absolute hydrochloric acid (hydrogen chloride) and 10 per cent. sodium chloride.

(*b*) By immersion for not less than 40 hours in a solution containing 1 per cent. absolute hydrochloric acid (hydrogen chloride) and 10 per cent. sodium chloride.

(*c*) By immersion for not less than 24 hours in a solution containing 1 per cent. formic acid, and mercuric chloride in the proportion of 1 part to 2,500 parts of the solution. Hides or skins treated by this process shall be held for 2 weeks following the treatment before neutralization.

(*d*) By immersion for not less than 48 hours in a 1 to 1,000 bichloride of mercury solution.

(*e*) By immersion for not less than 6 days in a 1 to 5,000 bichloride of mercury solution, plus not less than 5 days in lime of the usual strength for dehairing.

or, in lieu of disinfection by one of the foregoing mentioned processes, the effluent shall be subjected to treatment by one of the following methods:

(*f*) Heat the effluent from soak vats, mill-drums, breaking machines, or other similar equipment, to a temperature of 100° C. (212° F.) and maintain at that temperature for at least one minute.

(*g*) Treat the effluent from soak vats, mill-drums, breaking machines, and other similar equipment with chlorine, in such manner and in such amount (not less than 250 parts per million) as to secure efficient disinfection.

(*h*) Subject the effluent from soak vats, mill-drums, breaking machines, and other similar equipment, to filtration, the effluent from the filters to be treated with chlorine in sufficient amount and in such manner as to secure efficient disinfection, provided, however, that in this method of treatment the sludge which collects on the filters shall be sub-

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jected to disinfection by heating at a temperature of not less than 100° C. (212° F.) for not less than 15 minutes.

(*i*) Treat the effluent from soak vats, mill-drums, breaking machines and other similar equipment with 50 parts of chlorine per 1,000,000 parts of effluent and heat at not less than 80° C. (176° F.) for not less than 30 minutes.

(*j*) In the case of sheep skins and goat skins, until further notice, by immersion for not less than 12 hours in a solution of milk of lime containing the equivalent of 5 per cent. of calcium oxide (CaO).

III. DISINFECTION OF GLUE STOCK.

All fleshings, hide cuttings, and parings or glue stock shall be moved from the port of entry to an establishment having proper facilities for the sanitary control and disinfection of such materials, in cars or approved containers sealed with either department of agriculture or customs seals, and upon arrival at the establishments, disinfected before removal therefrom by one of the following methods:

1. By heating in water at a temperature of 100° C. (212° F.) for not less than 15 minutes, or by heating in water at a temperature of not less than 82° C. (180° F.) for not less than 4 hours.

2. By soaking in milk of lime or lime paste for not less than 24 hours.

3. By soaking in water containing not less than 2 per cent. of absolute hydrochloric acid for not less than 20 hours.

4. By soaking in water containing not less than 1 per cent. of absolute hydrochloric acid for not less than 40 hours.

IV. DISINFECTION OF BONES.

1. All hornpiths and porous bones classed as glue stock must be moved from the port of entry to an establishment having proper facilities for their sanitary control and disinfection, in cars or approved containers sealed with either department of agriculture or customs seals, and upon arrival at the establishment, disinfected before removal therefrom, as provided for glue stock.

2. Bones with pieces of hide or tendons attached and all other bones not otherwise provided for shall be moved from the port of entry to an establishment having proper facilities for their

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sanitary control and disinfection, in cars or approved containers sealed with either department of agriculture or customs seals, and upon arrival at the establishment, disinfected before removal therefrom by one of the following methods:

(*a*) By heating in water at a temperature of 100° C. (212° F.) for not less than 15 minutes.

(*b*) By heating in water at a temperature of not less than 82° C. (180° F.) for not less than 4 hours.

V. DISINFECTION OF HOOFS AND HORNS.

Hoofs and horns shall be moved from the port of entry to an establishment having proper facilities for the sanitary control and disinfection of such materials, in cars or approved containers sealed with either department of agriculture or customs seals, and disinfected before removal from the establishment by heating in water at a temperature of not less than 74° C. (165° F.) for not less than 15 minutes. Bones removed from horns and hoofs that are required to be disinfected, shall be handled as provided for glue stock.

VI. DISINFECTION OF CONTAINERS OF GLUE STOCK, BONES, HOOFS AND HORNS.

Containers of glue stock, bones, hoofs and horns, which under the provisions of regulations III and IV of Joint Order No. 2, are required to be disinfected, shall be handled as follows:

(*a*) The containers shall be burned, or

(*b*) The containers shall be subjected to moist heat at a temperature not less than 100° C. (212° F.) for not less than 15 minutes.

VII. DISINFECTION OF HAY, STRAW, ETC.

Hay, straw, or similar materials, shall be placed in a compartment made tight by sealing all crevices therein and then subjected to treatment with formaldehyde gas applied as follows:

The formaldehyde gas shall be generated from solutions of formaldehyde containing not less than 37 per cent. actual formaldehyde by pouring the formaldehyde solution on to pulverized potassium permanganate, the formaldehyde solution and the

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potassium permanganate being employed in the proportion of 20 ounces of formaldehyde solution by weight and 16-2/3 ounces of potassium permanganate by weight to each 1,000 cubic feet of space in the compartment to be disinfected. Bales of hay, straw, or other material shall be piled in block so that not more than 6 inches of any surface of the bale is in contact with another bale, or if deemed necessary by the inspector, the bales shall be broken and the straw or hay loosened, so that a satisfactory penetration of the formaldehyde gas may be obtained. The disinfection with formaldehyde gas shall be carried out in compartment in which the temperature is not less than 65° F.

J. R. MOHLER,
Chief of Bureau of Animal Industry.

SOLE LEATHER ANALYSIS.*

By Oskar Riethof.

In the last few months many sole leather tanners who never did so before have had their leather analyzed in order to see how their stock compares with the army specifications.

There is no difficulty in comparing the results of a sole leather analysis with the Government limits; but a complete leather analysis is and should be of great interest in many other respects. The chemist of a large corporation with a well-conducted laboratory believes it his duty to assist the tanner in making the best possible use of every analytic report leaving his desk, and, in fact, he will be very much pleased to give any further information desired, because it stimulates him to greater efforts when he sees that the results of his work are put to good practical use. The smaller concerns that employ the services of a leather trades chemist only occasionally are often satisfied to get the reports, without comment. If the report of an analysis is not fruitful in the hands of the tanner, the chemist cannot be blamed, because he cannot be expected to know whether or not his customer's training enables him to make full use of the different figures of the report. He will not volunteer advice for fear of offending the tanner, and will confine himself to such information as is requested. In such a case the chemist is in the same predicament as the man who attempts to write for publication on a general

* *Hide and Leather*, Jan. 5, 1918.

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technical subject, like the writer of this article. He will always be afraid of saying something that everyone knows, or ought to know, and will feel like apologizing after every line. It thus happens that we have ample opportunity for reading articles on the most difficult subjects, but are often unable to find any information in regard to the most common problems.

Analyzing an Analysis.

In the following lines we will try to "analyze" an analysis of vegetable-tanned sole leather in order to show what the various items of a report really mean, and what can be learned from them in regard to the character of the leather in question.

The report blanks used by the members of the American Leather Chemists Association are quite uniform, in some instances varying only in detail. This non-conformity may be eliminated in the near future by a concerted action of the American Leather Chemists Association.

The results of the analysis of American standard tannages are, on the whole, confined between surprisingly narrow limits, showing that all over the country standard processes seem to be in use.

Below is given a type analysis of oak and union leather, upon which we will base all further explanations.

LEATHER AS RECEIVED.

	Per Cent.
Moisture	10.50
Oil	3.00
Insoluble ash	.20
Hide substance	34.50
Combined tannin	27.60
Uncombined tannin	10.40
Soluble non-tannins	13.80
	100.00
Total ash	1.50
Water soluble material	24.20
Degree of tannage	80.00
Leather substance	62.10
Sugar as glucose	4.00
Magnesia as Epsom Salts	3.00
Free acid as sulphuric	.50
Specific gravity	1.02

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Army Specifications.

It will be seen that the above analysis conforms with the newest army specifications of October 16, 1917, which are as follows:

"Moisture not to exceed 14 per cent., ash not to exceed 2 per cent., oil and grease not to exceed 5 per cent. nor less than 2 per cent., free acid not to exceed 1 per cent., water solubles not to exceed 30 per cent., glucose and magnesia present (the latter calculated as Epsom salts) shall not be more than 30 per cent. of the total and that the Epsom salts present shall not be more than 50 per cent. of the total amount of glucose and salts. That in form of bends, backs or sides the leather shall be sampled by taking a cutting along the edge of the back, this sample to be 2 inches wide and not over 8 inches long; the center point of sample shall be a distance of 24 inches from the root of the tail."

It seems that since the publication of these modified specifications, tanners are sending to their chemists one oblong piece of leather the required size. To the writer it seems preferable to get several pieces cut from different hides, because this will undoubtedly give a better average sample of the stock. Furthermore, the pieces should not be cut with square corners, since it certainly does not improve the looks of a side to do so. It will answer the purpose just as well to cut a crescent-shaped piece in the same manner as tanners are accustomed, provided the piece is 2 inches wide in the center.

Moisture.

The percentage of moisture in leather that is properly dried will hardly ever exceed the government limit of 14 per cent. It will average about 10 per cent. and the laboratory will generally show a somewhat lower percentage than the leather has in the store room, because the sample will dry out some before it reaches the laboratory.

Oil.

The percentage of oil in leather is found by extracting a weighed quantity of the finely ground sample, with petroleum ether. From 2 to 3 per cent. of oil is the average found, and this is generally sufficient to make the leather pliable and of

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good color, without causing oil stains. As the sample is taken from the firmest part of the side, the softer parts naturally will show a higher percentage of oil than the sample analyzed. Without a special request from the tanner, the chemist will not specify the kind of oil found. But if desired, there is no difficulty in giving the percentage of mineral oil.

The question of the influence of sulphonated oils on the quality of leather, especially on its water resistance, is still open and will not be dealt with at this time.

Water Solubles.

After the oil is extracted from the sample, the water soluble materials are determined by soaking the leather over night, and in the morning extracting the soluble part with a certain volume of water at 50° C., in 3 hours. This extract contains the soluble tannin and non-tannins, the latter including sugar and Epsom salts. The government maximum of 30 per cent. water solubles is certainly high enough and will seldom be exceeded. The average seems to be about 24 per cent.

Leather Substance.

When we have determined the moisture, oil and water solubles in leather we have the pure leather substance left, together with such insoluble mineral matter as constitutes the insoluble ash. All the above constituents, then, when added, will give a total of 100 per cent. The leather substance consists of the hide substance and the combined tannin.

Insoluble Ash.

The insoluble ash is in most cases only about 0.2 per cent. If it is much higher, it indicates that the leather was weighted with insoluble salts like barium sulphate, lead sulphate, kaolin, etc., and the chemist, if requested, will be able to tell the reason for the abnormally high value.

Hide Substance.

The percentage of hide substance is of very great interest, be-

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cause we can draw conclusions as to the yield of a certain leather —the higher the percentage of hide substance, the lower the yield. Well tanned sole leather will show between 32 and 40 per cent. hide substance, depending to a great extent upon the degree of filling.

A great number of leather analyses collected by the writer from different sources[1] seem to indicate that the average so-called oak leather has the highest percentage of hide substance, followed by union and hemlock leather; the yield therefore being in opposite direction. But there are so-called oak leathers on the market which show a higher yield than many union and hemlock tannages.

If the question arises as to whether or not some oak bark has been used in tanning a certain leather, the chemist will be able to give this information. He can also tell if sulphite-cellulose extract has been used.

The analysis made from a sample taken according to the government specifications does not represent the average of the whole hide. This does not impair the value of the analysis, however, because we will get comparative results no matter where the sample is taken from, provided all samples are cut from the same place. But it is important to remember this when drawing conclusions from an analysis, and must be remembered by the tanner, sole cutter or shoe manufacturer, who may send a block, strip or cut sole to the chemist and attempt to compare the results of the analysis with those obtained from leather sampled according to government specifications.

How great the difference in the same bend may be, depending on where the sample is taken from, can be seen from the following two sets of analyses of union leather, which represent the average of a series carried on by the writer some time ago. The samples marked "back" were taken from about the same place as provided in the new government specifications, the shoulder samples from the shoulder end of the bends and the belly samples from the belly part of the bends.

[1] This JOURNAL, July, 1917.

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I. LEATHER AS RECEIVED.

	Back.	Shoulder.	Belly.
Moisture	11.31	10.64	11.38
Oil	2.33	4.30	3.97
Insoluble ash	.18	.17	.17
Hide substance	31.86	28.77	27.85
Combined tannin	29.61	30.78	29.20
Uncombined tannin	8.79	8.88	8.69
Soluble non-tannins	15.92	16.46	18.74
	100.00	100.00	100.00
Specific gravity	1.09	1.06	1.05
Soluble ash	1.66	1.82	2.42
Water soluble material	24.71	25.34	27.43
Leather substance	61.47	59.55	57.05
Degree of tannage	93.00	107.00	104.90

II. LEATHER AS RECEIVED.

	Back.	Belly.
Moisture	8.82	8.68
Oil	3.12	4.86
Insoluble ash	.20	.20
Hide substance	33.89	28.45
Combined tannin	31.89	29.49
Uncombined tannin	8.94	11.34
Soluble non-tannins	13.14	16.98
	100.00	100.00
Specific gravity	1.03	.99
Soluble ash	1.41	2.08
Water soluble material	22.08	28.32
Leather substance	65.78	57.94
Degree of tannage	94.10	103.70

Similar experiments were carried out by Paessler, Appelius and Manstetten,[2] Oberfell,[3] and others. Paessler found that the neck gives the best average, and this is borne out by the results of the other investigators.

Estimation of Yield.

It would be futile to attempt to give a fixed rule for the relation between the percentage of hide substance of the back and the average of the whole hide, because this will depend to a

[2] Ledertechn. Rundschau, 1910.

[3] This JOURNAL, 1912, p. 27.

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certain degree upon the class of hide, the tanning process and the extent of filling, but for a certain plant it is not very difficult to establish the average percentage of hide substance in finished leather. Once obtained, this figure is very useful for the estimation of the yield a certain lot of hides should give. To do this we have to know the percentage of white weight and the percentage of dry hide substance in the pelt. The last named figure must be established for each plant separately, since it will be influenced by the quality and temperature of the water, and to some extent by the class of hides.

The relation for the estimation of the yield is as follows:

$$\frac{\text{Per cent. white weight} \times \text{per cent. hide substance in pelt} \times 100}{\text{per cent. hide substance in finished leather}} = \text{estimated yield.}$$

Sometimes there will be a small difference between the estimated and the actual yield, but on the whole it works out quite satisfactorily.

Degree of Tannage.

We mentioned before that the hide substance plus the combined tannin gives the leather substance. The higher the ratio of combined tannin to the hide substance, the better the leather is tanned. Schroeder, the father of leather analysis, introduced the expression, "degree of tannage," or "tannage number," which expresses the parts of tannin combined with 100 parts of hide substance. For the backs of well tanned sole leather, this factor is ordinarily between 75 and 85. In the looser parts of the side it is generally considerably higher, as can be seen by comparing the results of the back, shoulder and belly in the above stated analysis. This again points out the necessity of cutting the samples from a certain well defined part of the hide.

Total Ash.

The total ash, as the name implies, consists of the insoluble ash and the soluble ash, the latter forming part of the water solubles. It may include in dry form magnesium salts, Glaubers salts and any other salts that were present in the extracts, etc. As Epsom salts contains about 50 per cent. water, and besides, loses more or less sulphur trioxide in ashing, the ash figure may be comparatively low, even if the leather contains a considerable amount

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of Epsom salts. A high total ash, when the percentage of Epsom salts is not abnormally high, indicates the presence of other mineral matter, as Glauber salts, barium chloride and others.

Specific Gravity.

The writer dealt with the value of the specific gravity figure for judging sole leather in a paper published in this JOURNAL, September, 1915. To repeat its contents here and in a few words, the specific gravity shows the relation between volume and weight; or in terms of the sole cutter, the cutting value. All other conditions being the same, the leather with the lower specific gravity will cut cheaper. This certainly does not take into consideration the result of grading the soles, as influenced by the rolling, cuts, tick marks, etc.

It may be well to point out the difference in the specific gravity of back, shoulder and belly as shown in the preceding table.

It is a matter of commendation that the sole leather specifications have been changed in September to what they are now, because the low percentage of sugar and Epsom salts of the former would have increased the specific gravity and so have lowered the cutting value of such leather, without improving the quality. There is no difficulty in making good sole leather without using sugar and Epsom salts, and without loading with other materials. But what such leather would cost per sole and how it would work on our Goodyear machines is another question. There was a time when the tanner who used salts and sugar even in moderate quantities was considered a highway robber, but fortunately such times have passed.

Free Acid in Leather.

The present methods for the determination of free acid in leather are not very satisfactory. There are different methods in use, every one of them giving reliable results under certain conditions, but all break down under special conditions. The Procter-Searle method is the one used by most chemists in this country, but even conceding that it is better than some of the others, the results must be noted with reserve.

The Government specifications limit the amount of free acid,

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mineral and oxalic, to 1 per cent. and such percentage seems high enough to take care even of possible discrepancies in our present methods.

Acknowledgment is hereby made of the valuable assistance of Mr. Charles T. Gayley.

Richwood, W. Va.

PICKLING AND TANNING SHEEPSKINS.*

By H. A. Abbott.

The pickling process of all light skins before tanning becomes more important every day. It is well to look upon it from two standpoints—first, as a method of preserving the skins before tanning; and, secondly, as an actual process in the tanning between the "wet work" and tanning proper. To follow the dry imported sheepskin from the animal's back to the time it reaches the warehouse is to note that it is submitted to three separate drying operations, *viz.*, in the place of its origin before packing into bales; after de-wooling; and after tannage, becoming in the "crust" state. Every process of drying lessens the tenacity of the leather.

The preliminary drying of the skins, before packing into bales for export, cannot be avoided, and, of course, the drying to the crust state is not so injurious because the tanned fibers have greater resistance than the nontanned fibers. It is, however, possible to avoid the drying after de-wooling, and this by means of the pickling operation.

The ordinary process of making pickled sheepskins consists of removing the wool with sulphide of sodium or other depilatory compound, liming a few days in weak clean lime liquor, drenching or puering, and then pickling with acid and salt. Usually there is plenty of sulphide of sodium in the skins when they are put into lime, and as the lime and drench do not remove all the sulphide, some is left in when the skins are pickled, and the acid in the pickle, acting upon the sulphide, makes the skins tender.

The toughest skins are secured when the sulphide is entirely removed before the liming process. The pelts are usually first

* *The Leather World*, Dec. 13, 1917.

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soaked in water containing borax until they are soft and clean, then drawn and pressed until all the dirty water is got rid of, otherwise imperfect grain is a result. Painting with the depilatory should be done very carefully to avoid any damage to the wool, and the strength should be sufficient to get the wool off with one application.

Market skins should be soaked as quickly as possible, and a plentiful supply of soft water should be used; a running soak gives the finest results. The chemicals that can be used for facilitating the process, particularly in the case of dried goods, are few, since due consideration must be taken of the fact that many of those usually employed in the soaking of other dried skins—*e. g.*, calf and goat—are not permissible in the case of wool skins, owing to the destructive action on the wool fiber. Bisulphite of soda gives excellent results, and a safe quantity to use may be reckoned at 4 pounds to 1,000 gallons of water, when the soaking should be complete in 2 days.

Following the pressing, if necessary, additional softening can be achieved by "breaking" the skins over on the beam, but this should on no account be attempted before the goods are pliable. After the wool has been removed dissolve 1 pound of bicarbonate of soda in warm water for each dozen skins, and wash them in a drum in this solution for 1 hour; then wash 2 hours in a paddle wheel with clear water to remove all the sulphide. The skins can now be placed in lime liquor; the lime should be weak and clean, and can be used either in a paddle or pit, extending to 4 or 5 days.

In the puering or drenching operation one runs up against prejudices both for and against the use of animal excrement, and puering substitutes. From whatever source the use of the former originated, it is just as safe to say that the method in its application is as successful as it is repulsive. However, to dogmatise on this theme is to lose time. Each puerman may have his speciality, but, after all, the ruling factor in either case is largely the skill and judgment in their separate use. An alternative course is drenching on the American plan by taking 50 pounds of grape sugar and dissolving it in 18 gallons of hot water. Let it stand in a warm room for 2 days to become soured. Heat water in a paddle vat to 95° F., and add 1 pint of the solution

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for every 500 pounds of pelt; add also 1 gallon of lactic acid, and stir the drench thoroughly. Paddle the skins for 3 hours in this drench, and then wash thoroughly in warm water, and put the goods into pickle.

In most methods of pickling, the skin is first submitted to the action of an acid liquor to which salt has been added, and after running in this bath for a variable time, it is treated in a very strong solution of salt. To start a new pickle dissolve 40 pounds of salt for every 100 gallons of water in the vat; then add 10 pounds of salt and 1½ pounds of sulphuric acid for every 100 pounds of pelt, weighed after washing from the drench. Paddle for 2 hours, then horse up for at least half a day. Formic acid can be used instead of sulphuric. Put the skins into a weak acid bath of 1 pound to 25 gallons of water, and leave until permeated with it, then pass into a stronger solution.

The natural grease should as far as possible be removed while the goods are in a pickled condition. Wringing and pressing are the methods in common use. When it is advisable to remove the acid, a drench of sour bran and salt should be used.

Skins treated as described tan rapidly and uniformly, and when finished are tougher and of better color than skins hurriedly rushed through the lime and drench, and pickled while they contain considerable sulphide of sodium.

A well-tanned leather is obtained by tanning the skins in a quebracho liquor to which some alum and salt have been added. The sulphuric acid should be removed before the goods are placed in the first liquor of the process. To make the first liquor take 350 gallons of water, and add to it enough dissolved quebracho liquor of 6° strength, and the skins should be turned in this for 36 hours, the liquor then strengthened to 10° strength, and the skins left in 2 days or until completely tanned.

The goods can now be washed and cleaned in a solution of sumac (2 per cent. in sufficient water to drum nicely) for ½ hour. One half per cent. of tartar emetic dissolved in hot water is now added, and the leather drummed ½ hour longer. For soft leather the skins can be fat-liquored, dried, and finished as may be desired.

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FUR AND FUR DYEING.*

By B. R. Armour.

President of the American Aniline Products, Inc.

Furs and fur dyeing are most interesting subjects.

The very mention of furs conjures up visions of arctic wastes, mountain crags, and tropical jungles, where tireless trappers brave danger and death to snare the skins that wrap milady's white shoulders, or are trodden upon disdainfully by her careless feet.

On the other hand, while not exposed to the hardships and dangers of the trapper, the fur dyer also must know the homes and habits of fur-bearing animals. With this knowledge, Mr. Fur Dyer attains greater skill in handling the furs, and "the leopard is made to change its spots."

A writer of romantic fiction might obtain many a profitable inspiration by standing for a few hours in a fur dyer's shoes, for, prosaically enough, the dyer of furs may dip a skin in its chemical bath, but, he may be holding in his hands the key to a story of romance and adventure stretching from a Thibetian plateau to the boudoir of a duchess.

The fur dyer is professionally a man of business concerned with facts and formulas rather than with yearning visions of romance, or lonely, wild, and faroff places. As it reaches his hands the skin is a most unromantic object—hard, dry and drab. It is his business to make of it a thing of beauty. In order to do this, he must turn his attention from its romantic antecedents and confine himself to technical processes. "The length of time it has been off the animal's back" is a great factor in determining the best method of dyeing a skin, but the greatest factor is "from what part of the world did this animal come when enjoying life?" Therefore, his imaginative excursions into the habitat of the strange animal is made to determine which formula must be used in dressing and dyeing the skins he is handling. A number of these are necessarily preliminary to the actual dyeing, and the methods used vary according to the type and condition of the skin. These processes are called fur dressing.

Opossum, raccoon and skunk are very greasy pelts. Therefore,

* *Color Trade Journal*, December, 1917.

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the grease is first scraped from the flesh side; then drummed for several hours in damp saw-dust. Next put in a mixture of damp saw-dust and salt over night. Next day the skins are moved to the fleshing room and the excess flesh is scraped off. Now they are pickled in a bath of sulphuric acid and salt so the skin will be converted into soft, pliable leather. At the same time, this pickling bath plumps (or fills out) the leather and care must be taken that the leather is not made too thick, for, if too plump, the leather will not be adapted to the scissors and the needles of the garment maker.

The skins are then dried and again drummed in damp saw-dust. As all the natural grease has been removed from the skins, it is necessary to replace the natural with artificial grease in order to make it soft and pliable. Therefore, they are next put in a tramping machine containing grease, and such grease is tramped or pounded into the leather. The skins are then drummed again several times in damp saw-dust to remove all grease from the hair.

As minks, wild-cat, Australian opossum, marmet and wallaby are not as greasy as opossum, raccoon or skunk, it is unnecessary to scrape the grease from the pelts. Otherwise, the dressing is the same.

Rabbits are first soaked in water two or three days, then fleshed, then pickled in a mixture of alum and salt and are then ready for the dyeing operation.

It is here that the fur and the dyer establish their point of contact. The colors used for fur dyeing are not colors in the accepted sense—but oxidation colors. That is, they are products which develop on the fiber when treated in conjunction with such oxidizing agents as ferric chloride, permanganate of potash, bichromates, peroxide of hydrogen or any metallic salts. They permit of the dyeing of furs in a cold or lukewarm bath to yield fast brown or black shades ranging from the lightest tan to the deepest blue black. Should by any chance the temperature of the dye-bath be increased, the hair will be singed and the leather burnt and the entire fiber of the skin destroyed. Of late, however, the more technical dyers have been able to overcome the singeing of the hair by brushing with a solution of glycerine. The hair, however, will return to its singed state in a few

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months. If the leather is not too far gone, a brushing with egg yolk, sulphonated cod oil and glycerine will overcome the brittleness to a slight degree. The tensile strength of the leather, however, is practically lost. The products used in the following recipes are known as

Fur Brown P, yielding an intense reddish brown.
Fur Brown 2 G, yielding a yellowish brown.
Fur Black, yielding a dead black.
Fur Blue X, yielding a blue black.
Fur Black DB, yielding a blue black with an intense blue tone.
Fur Black DD, yielding a very deep blue.

It is impossible to give general recipes suited exactly for every kind of fur, for, as before mentioned, the properties vary according to the quality of the skins.

For instance, a recipe worked out to produce satisfactory results with foxes would produce most unsatisfactory results with rabbits. Therefore, the proportions can be determined only by trial. However, you will note peroxide of hydrogen is used in all the following formulas, and a very good basis for the application of hydrogen peroxide in proportion to color has been found to be 10 to 1. When in doubt use this ratio, for it can be varied when necessary. Also note that without exception the dyestuff must be thoroughly dissolved before adding the hydrogen peroxide, and unless otherwise specified, the proportions given are based on a 2-gallon dye bath.

All skins are "killed" before dyeing with such products as bichromate of potash, bluestone, copperas, verdigris, caustic soda, potassium chlorate, etc., and as usual, the methods vary according to the type and quality of the skin.

When making tans or browns, it is advisable to mordant the skins before dyeing with ⅓ ounce to 1⅓ ounces of the bichromate of potash and ⅓ ounce to 1⅓ ounces of cream of tartar according to the depth of shade required. The skins are immersed in this bath at about 75° F. and kept there for about 12 hours, or better still, over night. After mordanting rinse lightly or whizz. The skins are now ready to be entered into the actual dye-bath.

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A solution of

⅓ ounce Fur Brown P
1 gill hydrogen peroxide
⅓ tumbler ammonia

produces a light reddish brown, after the skins remain in the bath about 6 hours.

1 ounce Fur Brown
⅓ ounce Fur Black
⅓ ounce pyrogallic acid
1 pint hydrogen peroxide
¼ tumbler ammonia

produces medium to dark brown shades, according to the length of time the skins remain in the dye-bath. After 3 hours a beautiful medium brown is obtained, while the shade gradually becomes darker until at the end of 12 hours you have a full, rich, dark brown. After dyeing the skins are rinsed for several hours in running water.

Pyrogallic acid produces a rich yellowish shade, but is only used for toning purposes.

It should be noted that in such combinations as the last, that since Fur Brown produces an intense reddish brown, pyrogallic acid is added to throw the brown onto the yellow side, and the Fur Black is used to darken the shade.

Of course, these combinations given above can be changed to produce most any shade of tan or brown.

Fur Black is best employed by mordanting with bichromate of potash and cream of tartar in the same proportions as used for the tans and browns and then dyeing in a bath of

⅓ ounce to 1⅓ ounces Fur Black
1 gill to 1 pint hydrogen peroxide

for about 12 hours at 75° to 80° F., rinsed, etc.

Fur Blue X without a previous mordant dyes angora a deep blue black with an admixture of black in the following proportion:

⅔ ounce Fur Blue X
⅓ ounce Fur Black
1 pint hydrogen peroxide

The dyeing operation is the same as for Fur Black.

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For this class of dyeing (angora) the recipes mentioned for Fur Black and Fur Brown may also be recommended; though, of course, solutions must be varied according to shade requirements.

Furs such as marmet or opossum, for example, are best killed before dyeing either with lime or a soda solution. They may then be rinsed and mordanted with a solution of ⅔ to 1⅓ ounces of copperas and ⅓ ounce cream of tartar and then dyed as above. While such skins can be dyed without a mordant, such a mordant as that given above greatly improves the finished material.

Fur Black DB and Fur Black DD are employed only when particularly blue shades of black are desired. For these brands, however, as in the case of Fur Blue X, it is essential that the skins be mordanted or killed before dyeing.

Full shades of black of a bluish cast will be obtained by adding ⅓ to ⅔ ounce of Fur Black DB or Fur Black DD or Fur Blue X and 1 gill to 1 pint of hydrogen peroxide to the regular Fur Black formula.

Certain hairs of furs will not take fur dyes in a bath. These must be tipped. For tipping a black shade, Fur Black only is suitable. It is used in the proportion of ⅔ ounce Fur Black to 1 pint of water and 1 pint hydrogen peroxide; the latter being added directly before using.

To produce brown shades by tipping, Fur Brown is used in combinations. With solutions of 1½ ounces to 5 ounces per gallon a single tipping will produce an intense brown of a depth which formerly was obtainable only by a long tedious process. After tipping, the skins are placed in pairs hair side inward and allowed to remain that way for several hours, after which they are put in a cool place to dry.

A good soda bath for killing is made up by dissolving 2 pounds of sal soda in about 12½ gallons (100 pounds) of water. The skins are washed in this cold for 1 to 2 hours. A good soap bath is obtained by dissolving 1 pound of soap in 12½ gallons (100 pounds) of water and adding 1 pound of ammonia. The skins are washed in this for 1 to 2 hours and afterwards rinsed in cold water.

For a lime bath dissolve 15 pounds of powdered sal ammoniac and 4¾ pounds of sulphate of alumina to 50 gallons of hot or

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boiling water. To this add a solution of milk of lime which is made by adding 50 pounds of quick lime to 100 gallons of water. The milk of lime may be kept in a well-stoppered earthenware vessel, but should be stirred before using.

To treat furs with this lime bath the hair side is painted with a brush, and the operation is repeated twice or as often as is necessary to remove the grease in the hair. The skin should then be dried in a shady place as direct sunlight and too intense heat rob the hair of its elasticity and make the leather hard. The chalk dust remaining after the skins are dried is removed by beating and brushing.

Fur dyeings possess the disagreeable property of staining lighter materials with which they come in contact. This may be remedied by the following inexpensive process, which will make the colors absolutely fast.

The skins that have been dyed by steeping should be treated in a fresh bath to which has been added 1/60 ounce to 1/20 ounce of bluestone per gallon for light shades, or 1/12 ounce bluestone for dark shades. After a bath of 6 to 8 hours the skins are then rinsed and dried. For skins that have been tipped use a 5 to 10 per cent. solution of bluestone, varying the strength according to the depth of the shade. This is applied with a brush after which the skins are dried and tumbled in sand or saw-dust. If the application is correctly carried out and care is taken to vary the strength of the solutions according to the depth of the shade treated the tone of the dyeings will not be affected. The use of too strong solutions in tipping will change the shade entirely.

The rapid development in the production of fur colors in this country is one of the achievements forced upon us by the war. Before the war no fur colors were produced in America, for the simple reason that the selling price was lower than the possible minimum cost of manufacture. Germany sold to this country her surplus of such intermediates at or below cost. It is probable that she will resume this practice after the war. In that case American manufacturers will be obliged to drop the making of fur dyes. The ad valorem duty of 15 per cent. and the special duty of 2½ cents a pound imposed by the tariff law

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on this class of intermediates will not afford any effective protection.

It is argued by competent people that, in order to possess a thoroughly self-contained industry, not dependent in any essential upon foreign supply, this country must produce all the materials that go to the making of her finished articles. There is no questioning the desirability of such a condition. But it must remain impracticable so long as American producers in any line are not secured against a species of foreign competition which it is impossible for them to meet.

In August, 1914, there were no fur colors made in America. In October of that year we put up our plant, and in December we began to manufacture. We have succeeded in duplicating practically all the German fur dyes, without substituting; and to-day the demand of American fur dyes is being satisfactorily supplied. Created to meet an emergency, this particular feature of the American dyestuff industry will assuredly disappear when the emergency ends unless proper protection is accorded this branch of the industry. The question remains whether in the best interests of the industry it is well to allow it to disappear.

HISTORY OF TICK FIGHT.*

Advancing well beyond the half-way mark in freeing the South from the cattle fever tick, removing the Federal quarantine from cattle shipment in 70,754 square miles of nine Southern States, driving a broad wedge of tick-free territory through the tick lines to the Gulf of Mexico—the fight against the destructive parasite must count 1917 as its greatest year so far.

December 1, when 65,520 square miles—the largest amount of territory ever freed at one time—will be added to the liberated areas, will be the greatest day in the campaign since it was started actively in 1906, and it will be celebrated as such in the States and counties to which it will signalize undeniably long strides toward realization of the South's merited position as a cattle-raising country.

The governor of Mississippi, whose people have made their State the first touching the Gulf to be entirely rid of the cattle

* *Weekly News Letter*, U. S. Dept. of Agriculture, Nov. 28, 1917.

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tick, has designated December 1 a day of rejoicing in the Commonwealth. A celebration at Jackson, the capital, and others at county seats have been arranged. At these ceremonials congratulations on the achievement will be received from the United States Department of Agriculture and from governors of other States. Celebrations of the same character are to be held in the various counties freed from quarantine in eight other States—Alabama, Arkansas, Florida, Georgia, Louisiana, North Carolina, Oklahoma and Texas.

Faltering, slow, and uncertain at first, the advance against the cattle tick in 11 years has gained such impetus that it now literally is sweeping forward. There is now no doubt of final success and there are great hopes that the goal of "a tick-free South in 1921," which also will mean American territory entirely freed from the parasite, will be realized.

Ticks Long Have Infested Cattle in South.

Cattle in the Southeastern Atlantic and Gulf States have been infested with the tick since cattle first were introduced into those regions. It is thought probable the ticks were introduced into the country by cattle from Spanish herds. The history of the tick in the South is largely a history of the agricultural life of that section. In it are intertwined the great events of a century or more that have attended the transformation of the South from a wilderness into a wide and prosperous agricultural domain.

Ticks carry a fatal disease between cattle. Calves survive the effect of it, but very few older cattle live long when attacked for the first time. But for the fact that the calf that lives after the attack becomes partially immune, there would now be no cattle in the tick-infested portion of the South. Southern cattle always have caused disease among Northern cattle whenever they, carrying ticks, have left their home territory and been driven into or through adjoining territory. A notorious example of such driving occurred after the Civil War when Texas and Indian Territory cattle were driven into Colorado and Kansas, leaving death in their trails for the native cattle. This caused the "cowboy wars," in which it was sought to turn the cattle back by force of arms, and also caused the enactment of stringent State laws.

During these years of settlement the cattle tick had extended

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northward until its distribution was about coincident with that of cotton. From this vantage ground it was scattered by driveway and by rail into Northern markets and caused annual outbreaks of Texas fever, as the disease was then called, throughout the North. Legislation in various States sought to check the disease at that time, but, owing to ignorance of the manner of its spread, was powerless.

Finally, with the formation of the Bureau of Animal Industry of the U. S. Department of Agriculture in 1884, the Federal authorities, under authority of Congress, began the fight against the tick. The bureau first sent out agents to define the line between infected and noninfected territory, and in the annual reports of 1884 and 1885 several maps were published showing its location. The first order defining and mapping the quarantined infected territory was published in 1889. The driving or transporting of cattle from the infected to the free territory was forbidden, except for a short season in winter and except for immediate slaughter when transported by rail or boat and discharged into quarantine pens at certain recognized slaughtering centers. This constituted a quarantine which has existed with timely modifications ever since.

The beginning of tick eradication is traced to a meeting of the Commissioners of Agriculture of the cotton-growing States held in Raleigh, N. C., in 1899, when the North Carolina commissioner directed that the State's aim to improve the cattle industry by tick eradication be presented. From this beginning until 1906, 12 counties in North Carolina had been released from quarantine. The association of the Commissioners of Agriculture and various allied organizations, influenced by the eradication work of North Carolina and the results obtained by Federal, State, and other investigators, together with the growing necessity of ameliorating the effects of the boll-weevil invasion, prevailed upon the United States Congress to make an appropriation in 1906 to empower the United States Secretary of Agriculture to inaugurate a plan of co-operation with the authorities of Southern States in tick eradication.

In the Annual Report for 1907 of the Chief of the Bureau of Animal Industry it was stated: "Encouraging progress has been made in the eradication of cattle ticks from the Southern States.

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This work, which was begun in the summer of 1906 under an appropriation by Congress of $82,500 * * * is no longer an experiment. The results already accomplished demonstrate that the extermination of this costly pest is not only possible but practicable, though several years may be required for the completion of the work."

The years since that report have been years of meeting and overcoming obstacles until now, when the real magnitude of the task can be appreciated, it is certain that nothing can permanently hold up the work.

The story of the cattle tick (known scientifically as *Margaropus annulatus*), in relation to the part it plays as carrier of the tick-fever organism, is one of the most interesting in the annals of scientific investigation. It has been described by one writer as a "romance in pathology." It may be recalled that in the early days of our cattle-exporting trade the Texas longhorn was most prominent. It soon became known that these cattle, although apparently healthy themselves, caused a deadly disease in other cattle, the part played by the tick being at that time unknown and unsuspected. Hence the disease acquired the name of Texas fever. The tick, however, is no respecter of localities so long as they are suitable for its propagation, and tick fever occurs wherever the combination of infected ticks and cattle is present. The problem of combating the disease was undertaken soon after the Bureau of Animal Industry was organized in 1884, and a few years later the epoch-making discoveries of the bureau scientists led to the true cause of the disease being found.

The discovery that ticks can carry germs of disease from one animal to another was the first instance in which the important rôle of insects as carriers of disease was ascertained. From it arose new procedures in preventive sanitation. Since then the noxious rôles of various other insects have been learned; for example, mosquitoes carrying malaria and yellow fever; the rat flea, bubonic plague; the house fly, typhoid fever. Formerly no attention was paid to the carriers; only treatment of the patients was considered necessary. Now mosquitoes are screened out of buildings and exterminated; rats are killed; and house flies are screened, starved, and "swatted;" all of which has greatly reduced the number of victims of the mentioned diseases. The discovery

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of tick inoculation was made through the joint efforts of several members of the bureau staff.

PROGRESS IN TICK ERADICATION, JULY 1, 1906, TO DECEMBER 1, 1917.

Figures prepared by the Bureau of Animal Industry, United States Department of Agriculture, show as follows the progress in cattle fever tick eradication July 1, 1906, to December 1, 1917:

State	Counties infected July 1, 1906	Counties infected Dec. 1, 1917		Counties released		Area infected July 1, 1906	Area infected Dec. 1, 1917	Area released	
		Whole	Part	Whole	Part				
	No.	No.	No.	No.	No.	Sq. miles	Sq. miles	Sq. miles	Per cent.
Alabama	67	27	3	37	3	51,279	19,918	31,361	61
Arkansas	75	27	6	42	6	52,525	20,952	31,573	60
California	15	....	....	15	....	79,924	....	79,924	100
Florida	50	46	1	3	1	54,861	49,961	4,900	9
Georgia	149	79	....	70	....	57,438	35,324	22,114	39
Kentucky	2	....	....	2	....	841	....	841	100
Louisiana	63	49	2	12	2	45,409	37,824	7,585	17
Mississippi	81	....	....	81	....	46,362	....	46,362	100
Missouri	4	....	....	4	....	1,386	....	1,386	100
North Carolina	75	21	2	52	2	37,365	9,674	27,691	74
Oklahoma	[1] 61	22	10	25	14	47,890	22,377	25,513	53
South Carolina	44	10	....	34	....	30,495	8,619	21,876	72
Tennessee	42	....	....	42	....	16,987	....	16,987	100
Texas	198	154	3	41	3	191,885	142,918	48,967	26
Virginia	30	3	1	26	1	13,918	1,686	12,232	88
Total	956	438	28	486	32	728,565	349,253	379,312	52

[1] Of the 61 counties, 56 were wholly quarantined and 5 were partly quarantined.

A systematic study of Southern cattle fever, begun in 1888, developed that the disease, very similar to malaria in man, was caused by a minute protozoan parasite that invaded the red corpuscles of the blood and in acute cases destroyed them so fast that the spleen became clogged with débris from the blood, the liver filled with bile, and the red coloring matter of the blood was passed off with the urine. Intense fever developed and the animal usually died in from 1 to 4 days after first appearance of symptoms of illness. The death rate was usually low in herds with many young or insusceptible animals; among old cattle it ran as high as 80 or 90 per cent. It was further found that the disease was acquired soon after the young of the cattle tick—called seed ticks—attached to the cattle. Acquisition of the ticks was found to be governed by their life history, on which

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is based the science of tick eradication and also the rules of quarantine. The life history is as follows:

Adult ticks carried by cattle fall to the ground, and in about a week each female lays from 2,000 to 4,000 eggs, each of them carrying fever germs. Hatching in about 3 weeks of warm weather, but requiring a much longer time in cold weather, the seed ticks remain on the ground or on grasses, hungry and waiting for a chance to attach themselves to a cow or steer. Attaching themselves, the ticks hunt for places in the hide they can penetrate and, finding them, immediately begin to suck blood and to grow. Two immature stages of development precede the adult stage, when the males fall off the animal and die, and the females also fall off, but lay their eggs on the ground before they die.

The method of tick eradication found to be effective and now used almost exclusively is the arsenical dipping bath. This method will rid a county of ticks in a single season, it has been shown. For the method to be effective every cow and steer in the county must go through the bath once every 2 weeks during the season.

The ticks clinging to the cattle are killed by the arsenical bath. Those that attach themselves before the next bath are killed in that emersion before they have time to lay eggs. Those forced to remain in the grass die of starvation.

The dipping vat with arsenical dip was first used for tick eradication in 1909 by a Federal inspector in Alabama. He followed the method used in stockyards of dipping for scabies, and also the Federal system of oil dipping for animals carried in interstate commerce. Previous to 1909 swabbing and spraying by hand were the methods used in the intrastate work. The vat method has been found to be not only effective and speedy but to be inexpensive.

In September, 1917, 21,095 public or private vats were available in 10 Southern States. The work in 336,678 square miles of territory was supervised by 272 inspectors of the Bureau of Animal Industry, 351 State inspectors, and 1,209 county inspectors.

A powerful aid in the tick fight has been the passage of State laws enabling effective Federal co-operation. In 1906, when the first Federal appropriation to inaugurate a plan of co-operation with States was made, such laws were in existence in only 7 Southern States—Virginia, North Carolina, Georgia, Kentucky,

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Tennessee, Oklahoma, and California. Since then laws have been enacted in Alabama, Arkansas, Florida, Louisiana, Mississippi, South Carolina, and Texas. The only State affected by ticks and missing from this list is Missouri, in which only four counties were infected in 1906, and which is now completely free.

Federal co-operation does not mean that the National Government builds the vats nor supplies the money and materials with which to "dip the tick" and kill it. But it does mean that the Bureau of Animal Industry of the United States Department of Agriculture furnishes trained men to supervise the work of dipping and show the people of any county how to make a beginning. Appreciation of this co-operation is shown by the fact that every State and most counties in the tick regions have appropriated public moneys to take advantage of the scientific and practical knowledge placed at their disposal by the Federal Government.

To survey adequately the benefits from tick eradication a glance must be taken at the baneful effects of infestation. Cattle not only die from the fever transmitted by the tick but they lose greatly in blood, meat, milk production, and reproductive power. The ticks suck the blood that should go to make beef and milk; prevent sale of infested cattle outside the quarantine area except for immediate slaughter and at almost any price the buyer chooses to pay; and close the door to importation of better stock to improve the quality of a herd, for new cattle brought into ticky country are easy and luscious prey for the tick.

Benefits from tick eradication are told in hundreds of letters received annually by the Bureau of Animal Industry. The consensus of opinion in these letters indicates that on the average cattle freed of ticks are enhanced in value about $10 a head, weigh one-fifth heavier, grade one-fourth better, and are safe from cattle fever and from shrinkage on account of ticks. The letters also show that where the tick is dipped out the Southern cattle industry is growing, that there is more improved blood, that the milk yield of cows is increased about one-fourth, and that there is an increase of forage crops and silos.

Here are some reasons why, in the opinion of Department of Agriculture officials, tick eradication is important, especially at the present time, and why the fight now half won must go on to complete victory:

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(1) Good agriculture is dependent upon animal husbandry, and of the domesticated animals cattle are the leaders for fertilizer purposes; (2) the supply of beef is not keeping pace with the demand and must be increased to meet the needs of America and the allies in the war; (3) cotton production, menaced by the boll weevil, must be kept up by cattle fertilizer and must be supplemented by cattle raising in order that the cattle farmer may thrive and be able to raise cotton at all; (4) the cattle business of the South, long a negligible item in most States because of depression caused by the ticks, can be made the equal of that of any country.

The progress made so far in tick eradication is taken to mean that every square mile in the South will be freed from the cattle tick within a few years. From the areas released from tick domination and quarantine will go forth to the areas still infested not only the inspiration of accomplishment but also the practical help of the Federal inspectors released from work in the counties just freed and ready for labors in new fields.

TANNAGE OF DRIED EAST INDIA KIPS.*

By C. F. Barber and P. R. Barker.

It is surely the hope of all interested in the leather trade that something will be done in the near future to insure the possibilities of the tannage of a much larger quantity of East India dried kips in our own country than has been the case in the past. It is without doubt possible to obtain some of the supplies that formerly have been sent to Germany, and turn them into good leather at a price which will compete favorably with anything on the market, even in normal times.

Some may bring up the argument that it has been tried and given up as impossible, but the writers would go as far to say that the cause of this could be found in the lack of up-to-date methods and, arising from these, exceeding slow processes. It must, however, be understood that they are far from being in favor of some of the reputed quick methods, which consist mainly of drum tannage, and in practically all cases produce a quality of tanned hide inferior to what might have been obtained

* *J. S. L. T. C.*, October, 1917.

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had a little practical thought been given to the study of the process before entering upon it. It is, therefore, with the above in mind that the authors put forward the following moderately quick method of tanning, etc., which produces a first class article, though more suitable for the man who is tanning and dressing than for anyone selling in the crust condition. In the former case, when goods are usually sold by measurement, it is scarcely necessary to produce a leather containing excess tan in the form of water solubles, while in the latter these will add to the weight.

These goods are usually soaked back in batches of 150 kips for one day in clear water, then drawn up, opened out and put into clean water to which about 10 pounds of sodium sulphide is added. After 2 days in this they are drummed for 1 to 2 hours in a little water and are put back for 2 days more in sodium sulphide.

The hides should now be soft enough to put into lime, and are hauled up and put into old lime. The limes are worked on the three-pit system, none of them being more than 2 or 3 weeks old. After the old lime the hides are successively put into the medium and new limes, remaining 4 days in each of the three limes. To obtain good pelt weight it is necessary to haul frequently and plunge the pit well, also to avoid over-crowding the pit. After unhairing and fleshing weigh the pack in order to obtain the pelt weight, which for East India kips should be about 250 per cent. on the dry weight. After unhairing and fleshing the hides are divided into packs according to the capacity of the paddles used in the tannery. Deliming is carried out with formic and lactic acids, and bating with an artificial material at a temperature of 100° F. The goods are scudded as usual.

The tannage is performed in paddles and lasts about 6 days. The first paddle is made up to 12° B., with gambier or some other mild vegetable tannin, and synthetic tannin is added to bring the strength to 15° B. The barkometer strengths of the other paddles are 20, 25, 30, 35, 37° B. respectively. Each paddle is turned over every day and also strengthened up with 3 gallons synthetic tan liquor and 15 gallons new gambier liquor at 75° B. When a pack has been in the paddles for the required time, it is horsed up to drain, pressed by a hydraulic press to a sammed condition and dry drummed.

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If it is desirable to keep goods in the crust condition, they may be fat-liquored at this point in the drum with up to 7 per cent. of a suitable slightly acid fat-liquor, and then set out and dried, when goods of a really splendid color should result with a leather weight of 130-150 per cent. on the dry weight. If, on the other hand, the goods are required for memel sides, as they undoubtedly are at the present time, they should be split and shaved, then drummed for ¾ hour in a 5 per cent. solution of synthetic tannin, and dyed by means of nigrosine, logwood and a little copperas. More than ½ per cent. of the latter should never be used as there is no doubt that much of the crackiness and tendency for grain to strip, complained of by the R. A. C. D., is due to excess of iron being used in this process by some manufacturers, instead of relying more upon a good nigrosine or other acid dyestuff.

It is a matter of opinion as to whether at this juncture a fat-liquoring or drum-stuffing should be given. We prefer the latter, using a mixture of such materials as paraffin wax, tallow and degras. This mixture gives a much more water-proof product than that obtained by simply using a fat-liquor. The goods should then be set out on the drum-setting machine, and after samming reset by hand. They are then hung up until dry and when dry are buffed, whitened, printed, seasoned, grained up by the armboard or machine, and sorted into the different qualities. Below are the analyses of some leathers which have been analyzed in the rough-tanned state.

	Leather tanned by above process	English drum-tanned leather
Fat	8.7	9.4
Moisture	12.1	13.7
Total solubles	13.9	25.2
Hide substance	29.3	26.0
Insoluble	36.0	25.7

Dried E. I. Kips finished as dull sides, and analyzed after finishing:

Fat	28.4
Hide substance	31.8
Moisture	9.3
Total solubles	7.7
Insoluble	22.8
	100.0 Per cent.
Ash	1.2 Per cent.

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CORRECTION.

The article on Tentative Standard Methods for the Sampling and Analysis of Commercial Fats and Oils in the issue of this JOURNAL for January, 1918 was taken from the December, 1917, issue of the *Journal* of *Industrial* and *Engineering Chemistry*.

Through an oversight proper credit was not given for this article.

ABSTRACTS.

Tanners Institute Annual Report. The sixth annual report of the Tanners Institute at Pratt Institute, Brooklyn, has just been received. It gives a general statement of history, objects and results followed by a more detailed account of the work during the past year and an outline of the courses. There are two courses, both conducted with the co-operation of the National Association of Tanners. The first is a 9 months' practical course in tanning and is designed to give training in the art of tanning and finishing different kinds of leather, and to supply a broader knowledge of the principles involved in these processes than can be obtained under ordinary conditions of commercial manufacture. The need for training of this sort is now well recognized, and men who have the advantage of the course here offered will find themselves fitted to advance rapidly to positions of greater responsibility. The course is open to men already employed in the leather industry who desire to increase their efficiency and also to students of ability and character from high schools, who, although without practical experience, desire to equip themselves for positions in the tanning industries, and who can give evidence of their ability to pursue the course with success. The plan of instruction followed makes it possible for each student in this course to become familiar with every detail of the tanning and dressing of leather by actual work in the Institute's tannery. This plant is equipped with modern machines for leather production on a scale sufficiently large to render the processes and results thoroughly reliable from the point of view of the commercial tanner. Completely appointed laboratories provide for training in the principles of elementary chemistry, and in those branches of analytical and technical chemistry that have special application in the manufacture of leather. The instruction given is sufficiently comprehensive to impart to the student a thorough working knowledge of the chemical processes involved in the art of tanning. There is also included in the course a considerable amount of instruction along mechanical and electrical lines, especially adapted to the needs of these students. Practical instruction is given in the operation of engines and electric motors, and in the principles and installation of steam piping, electric wiring, belting, shafting and gearing. The work in drawing has direct reference to the design and arrangement of tannery plants and their equipment.

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The second is a nine months' post-graduate technical course in Applied Leather Chemistry. It offers to those who have had a thorough training in chemistry opportunity for specialized study in the principles and practice of tanning and in the chemistry of leather manufacture. Pratt Institute possesses unrivaled facilities for training of this kind, and provides exceptional opportunities for post-graduate students who desire to qualify themselves for technical positions of responsibility in the tanning industry. The course of study is not only advanced and thorough on the chemical side, but is conducted in close relation to the practical requirements of the tannery. Instruction is given in the manufacture of leather in all its branches, and practice is afforded in the actual tanning and finishing of leather under conditions that approximate closely to those obtained in modern establishments. The inspection and study of typical tanneries constitute an important feature of the course, and exceptional opportunities are given for observing leather manufacture as conducted in this country. The expense of trips to distant points is met by the Tanners Institute Fund. Special instruction is provided in the chemistry of leather manufacture and in other closely related branches of industrial and technical chemistry, such as dyeing and the testing of dyes, soap making, leaching, the manufacture of chemicals, oils, extracts, and other materials entering into tanning operations. A study is made also of the design of tanneries and their equipment, and problems in the supply of power, heat and steam and the handling of materials are worked out in detail. In the mechanical and electrical laboratories special attention is given to the subject of steam and electrical power machinery and the transmission and application of power. In addition to the regular work of the course, a series of lectures on technical and economic problems relating to leather manufacture, is given each year by experts and specialists in various departments of the tanning industry. The Institute tannery affords opportunities for making comparative tests of various leather manufacturing processes, and the Tanners Institute Fund provides funds for conducting original investigations in various problems of the trade. The principal subject for experimental investigation during the year 1916-1917 was the Progressive Rate of Tanning, a study of the degree of tanning at various stages of the process. This investigation, which extended over a period of several months, was under the direct supervision of Dr. Allen Rogers and his assistants. The valuable data obtained from this study will be reported to the National Association of Tanners.

A class of fourteen were graduated from the Tanning course and two from the Applied Chemistry course. The demand for young men with Tanners Institute training was so great that all members of the Class of 1917 were placed in good positions at least one month before graduation, and many more might have been placed had they been available.

The Prevention of Waste in Fats. *The Leather World,* December 20th, 1917. In an editorial attention is called to the great need of saving fats

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particularly in the leather industry. In Germany and France, where fats are under Government control, they are issued to tanners only when the resulting leather is to be used for military purposes. In Switzerland all scrap leather and cuttings are at the disposal of the Government for recovery purposes. English tanners are therefore urged to save everything that contains grease; scrap leather, cuttings, floor scrapings, etc.

Chemical Glass in Scotland. *Commerce Reports.* Some work had been done before the war along this line, but the country was dependent on Germany and Austria for their chemical glassware. As soon as the war broke out, operations were started on a large scale. Under the guidance of workmen from Belgium, men and boys were trained and work was under way as early as January 1915. In addition to the commoner chemical glassware, they are making apparatus for nitric acid manufacture, gauge glasses, glass for miners safety lamps, etc. British scientists have proven by exhaustive tests that this glassware is superior to the best German makes.

War-time Tanning Extracts. Felix Abraham. *J. S. L. T. C.*, Nov. 1917 from *Collegium*, 1917, pp. 161-166. Much difficulty has been experienced in Germany with the manufacture of leather by means of the available tanning extracts there, which are being prepared from native tanning materials. The troubles are all attributed to the bad quality of these war-time extracts, and this in turn is variously attributed to the unsuitable preparation, bad extraction or careless choice of raw materials. The author provides data showing the very much larger proportion of non-tans in the materials and extracts now available, (*e. g.*, pine bark, oak bark, oakwood, chestnut wood), as compared to pre-war materials, especially quebracho. He contends that tanners have not taken this important factor into sufficient consideration, as shown by the way they are repeatedly using old liquors and strengthening them up. This causes accumulation of non-tans. The hide consists of the finest individual structures. The molecules of tannin penetrate to the interior of the hide and thus effect tannage. The molecules of non-tans also penetrate the hide and exert an outward pressure which becomes so large with high percentage non-tan content that further penetration of tannin is rendered difficult or impossible. So long as the pressure of the tan outside is greater than that of the non-tans in the hide, tannage will proceed quite smoothly. In the coloring liquors or suspenders tannage proceeds quite regularly, but by increasing the non-tans (by adding fresh extract) the liquors become so saturated with non-tans that a very poor tannage is effected. Coloring liquors should be thrown away as soon as chemical analysis reveals a very low and negligible tannin content. Baumé or barkometer readings are no guide for this purpose. Hides should be tanned right through in the coloring liquors and not left for the drumming to complete penetration. The author is certain that attention to these details will obviate all difficulties with war-time extracts.

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The Bark and Wood of the Sweet Chestnut. J. Paessler. *J. S. L. T. C.*, Nov. 1917 from *Collegium*, 1917, pp. 130-141, pp. 167-176. Previous to the war, the wood of the sweet chestnut (*Castanea Vesca Gaertn*) was only of importance as a raw material for French and Italian extract manufacturers. The sweet chestnut grows very quickly and can be utilized for its tannin content when 10-15 years old. With chestnut trees, the tannin content of the wood increases with age. Unlike oakwood, chestnut wood from trees 12-18 years old contains sufficient tannin to merit its use for extract manufacture, but older wood is preferable. Further, the sapwood contains almost as much tannin as the heart wood. The bark is also rich in tannin, hence during the war, the bark and wood have been broken up together for extraction. Fresh chestnut wood containing 35-45 per cent. water shows 3-11 per cent. tannin by the filter process, varying according to its use. The tannin content of chestnut wood is appreciably higher than that of oakwood from trees of the same age. Data are provided from trees varying in age from 13-71 years showing that the tannin content of the wood increases with age. By leaving the trees to reach an age of 15-30 years more wood will be obtained and a higher percentage of tannin in the wood. The tannin content of the bark of trees 47 years old is very large and compares very favorably with that of a good oak bark, and shows a similar proportion of tans to non-tans. The content of glucose and its proportion relative to the tannin content is as high as that for oak bark hence it can be inferred that the same amount of acid will be formed as with oak bark. The average tannin content is 11-12 per cent. and it may even rise to 15 per cent.

TYPICAL ANALYSIS OF ALSACE SWEET CHESTNUT BARK.

	Filter process		Shake process
Tans	11.2		9.7
Soluble Non-tan	6.8		8.3
Insolubles		67.5	
Water		14.5	
Glucose		4.3	
Other Sugars		0.5	
Total sugary matter		4.8	

PER 100 PARTS TAN.

Glucose	38	44
Other Sugars	4	5
Total	42	49

No generalization can be formed about the variation of the tannin

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content of the bark with age except that it is very high even in the oldest trees. This is unlike oak bark where the corky layer starts forming after 16 years growth and causes a diminution in tan. The tannin content of the bark is the same at different heights of the chestnut tree thus providing an advantage over oak trees where it diminishes towards the crown of the tree. Consequently the average tannin content of chestnut bark is higher than that of oak bark.

According to the author's researches chestnut bark and its tannin appear to be exactly similar to oak bark and its tannin. The barks themselves closely resemble each other in appearance, smell, tannin and glucose contents, chemical reactions and so-called contents. Both yield a similarly colored tannage and darken on exposure to light, and chestnut bark is quite equal to oak bark in every respect. The author thinks that the leather industry should use chestnut bark to a greater extent. He strongly advocates replacing oak trees in Germany with sweet chestnut trees since the latter grow more quickly, yield more bark at an early age, and provide wood which can be used for its tannin content. Chestnut trees would thus be of more profit to the forestry people and to the leather trade. Various data are provided showing that by using both wood and bark three and one-half times as much tannin is obtained from chestnut trees as with the bark alone. Analysis shows that the prickly husk of the chestnut contains tannin 10.1-12.8 per cent., non-tans 3.2-16.3 per cent. which is a very appreciable tannin content, but the high non-tans percentage renders it useless for extract manufacture. The brown husk shows tans 7.3-8.8, non-tans 4.8-8.1. He thinks both may be worthy of consideration if great scarcity of tanning materials should arise.

A Method for Preventing Salts from Creeping Over the Sides of Evaporating Dishes. W. O. Robinson. *J. A. C. S.* Jan. 1918. In the course of mineral or soil analysis it is frequently necessary to evaporate saline solutions to smaller volumes or to complete dryness to expel ammonium salts. When, during evaportion, the solution becomes saturated and solids separate on the sides of the dish, the deposited solids, particularly if calcium and magnesium chlorides be present along with ammonium chloride, have a tendency to draw the less concentrated solution further up the sides of the dish and deposit crystals there. If determinations are left to run overnight or unwatched in the daytime, they are frequently ruined in this manner. Creeping can easily be prevented by painting a strip about ¼ inch wide around the inner rim of the dish with collodion. Salts will not creep over this strip. The collodion dries immediately after being put on so there is no time lost in this operation. The film contains no non-volatile residue and can easily be burned off.

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PATENTS.

Method for Treating Sewage. U. S. Patent 1,242,986. WALTER H. SAWYER, Auburn, Me. Method consists in dividing the organic matter in the sewage to fibrous and non-fibrous organic matter and removing and drying the fibrous matter.

Machine for Grading and Sorting Leather. U. S. Patent 1,243,260. CHARLES E. CLARKE and JOHN S. DELANEY, Winthrop, Mass.

Composition for Water-proofing and Preserving Leather. U. S. Patent 1,244,062. NORA MCLAUGHLIN, Seattle, Wash. A composition consisting by volume of paraffin, one part; turpentine, six parts; benzine, ten parts; oil of cloves, one-sixth part; oil of citronella, one-sixth part; oil of cedar, one-sixth part.

Artificial Leather and Manufacturing the Same. U. S. Patent 1,244,567. A. H. WHITMORE.

Artificial Leather. U. S. Patent 1,245,977. SADAKICHI SATOW, Sendai, Japan. Consists of glutinized vegetable proteids, and cellulose derivatives, a sticky viscid substance, fibrous material, a condensing agent and an alkali.

Artificial Leather. U. S. Patent 1,247,610. C. E. ARNOLD, Wilmington, Del. Consists of applying a cementing substance, which may be nitrocellulose and then a coating of plastic nitrocellulose by pressure, after the first coat is dry.

Vegetable Glue. U. S. Patent 1,248,039. R. W. TUNNELL, Philadelphia, Pa. Consists of hydrolyzed starch and an alkaline aluminate.

Leather Making Machine. British Patent 108,665. R. F. WHITNEY, Winchester, Mass.

Tanning. British Patent 108,796. J. E. MAUDE, Liverpool, England. Hides, etc., are supported on rods carried on flexible bands or chains passing around drums, wheels, etc., the hides being alternately immersed in the liquor and raised therefrom.

Making Leather. British Patent 109,977. W. COX, Wellington, New Zealand. A hide washing or bating machine.

Tanning. British Patent 110,470. A. TURNBULL and T. B. CARMICHAEL, Liverpool, England. Tanning materials are dissolved in a jelly formed of starch emulsion.

Leather. British Patent 110,509. A. O. TROSTEL, Milwaukee, Wis. A machine for embossing followed by buffing.

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33 members voted in favor of same.

7 members voted against same.

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ANALYSIS.

Tannin	Total solids .....
Non-tannins	Soluble solids .....
Insolubles	Ash .....
Water	Specific gravity .....
Total	Twaddell .....

Analyzed by the Official Method of the A. L. C. A. $\frac{\text{SLOWLY}}{\text{RAPIDLY}}$ Cooled.

THE WEAR RESISTANCE OF LEATHER FROM DIFFERENT PARTS OF THE HIDE.

By F. P. Veitch, Chemist in Charge, and *J. S. Rogers*, Assistant Chemist, Leather and Paper Laboratory, Bureau of Chemistry, Department of Agriculture.

What proportion of the 800,000,000 or more pairs of shoe soles used in this country each year, and which cost the people not less than $400,000,000, are so tanned that they give the purchaser the maximum of service, comfort, and satisfaction, is not known either to tanners or to leather investigators. The lack of definite knowledge on this subject is due to the fact that, up to the present time, no systematic investigations have been conducted which conclusively show the serviceability of different tannages of sole leather.

This matter is one which is not only of direct interest and importance to the public individually, but also to the tanning industry, and is one which that industry earnestly desires to see conclusively settled.

As a part of its general investigation on leather and leather production, the leather and paper laboratory conducted the preliminary experiments here described during the summer of 1913 in order to lay the foundation for larger and more extended investigations.

In determining the wear resistance of sole leathers there are, in general, two methods of procedure possible: actual wearing tests and tests made by a standardized wearing machine designed to give accelerated service. These experiments, which were conducted entirely by the former method, had as their objects the comparison of the wear resistance of leathers from different

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parts of the hide and of different tannages. The results obtained were to be used as an aid in the development of a standard laboratory wear-testing machine.

The following samples of leather were used:

Three differently finished sides of oak sole leather;
Three differently finished bends of oak sole leather;
One side of hemlock sole leather;
Bull heads (oak);
Waterproofed bull heads (oak);
Oak belting shoulders.

Soles were outlined and numbered on these sides and bends, and the leathers photographed before cutting in order to record the exact position of each sole (Fig. 1). One hundred and twenty-five pairs of bare foot sandals were manufactured, the soles being so combined that each pair represented two different leathers. After carefully measuring the thickness of the soles with a Vernier micrometer, the sandals were assigned to boy scouts in Hagerstown, Md., and Washington, D. C. Cards were issued on which the boys recorded the number of hours worn. Every two weeks the sandals were inspected, the soles measured, and new record cards issued for the succeeding two weeks. This procedure was followed until one of the soles for each pair was worn through. After the data for this sole had been recorded it was repaired in order that the test on the other sole might be completed. When both soles were worn through final measurements were taken and the worn sandals were photographed (Fig. 2).

There are many factors which play a part in the wear of sole leathers. Among these may be mentioned the characteristic walk of the wearer; the effect of weather conditions; of pavement or ground; of wearing out of doors or in the house or factory; distance walked; number of hours worn; difference between hides and variations in the same side of leather, etc. All of these and doubtless many other conditions exert their influence upon the wearing away of sole leather. For none of these factors, however, is it practical in a test of this kind to make a correction. The only hope for success in this type of experiment lies in averaging the effect of these conditions by making a very large number of tests.

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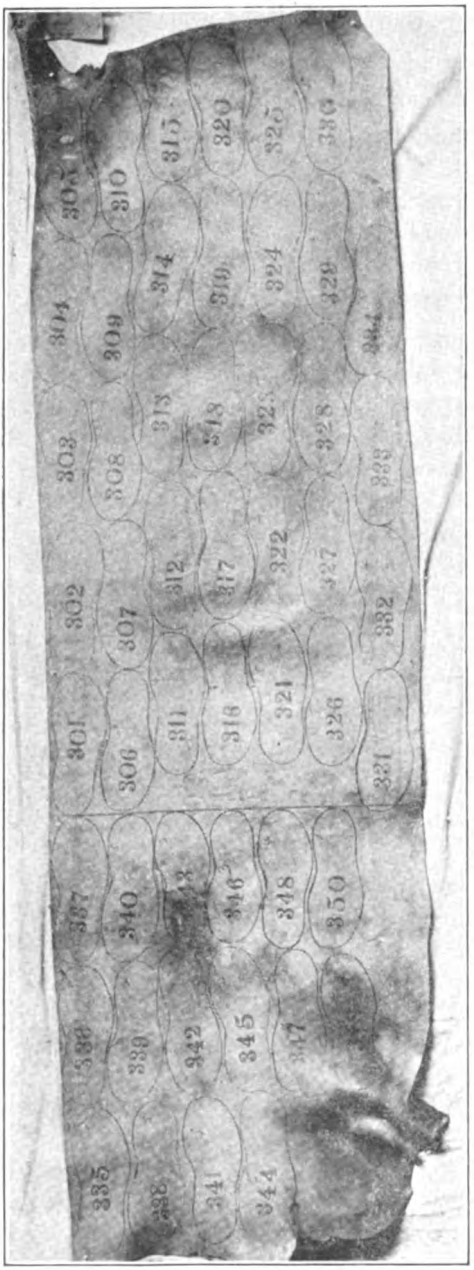

FIG. 1.

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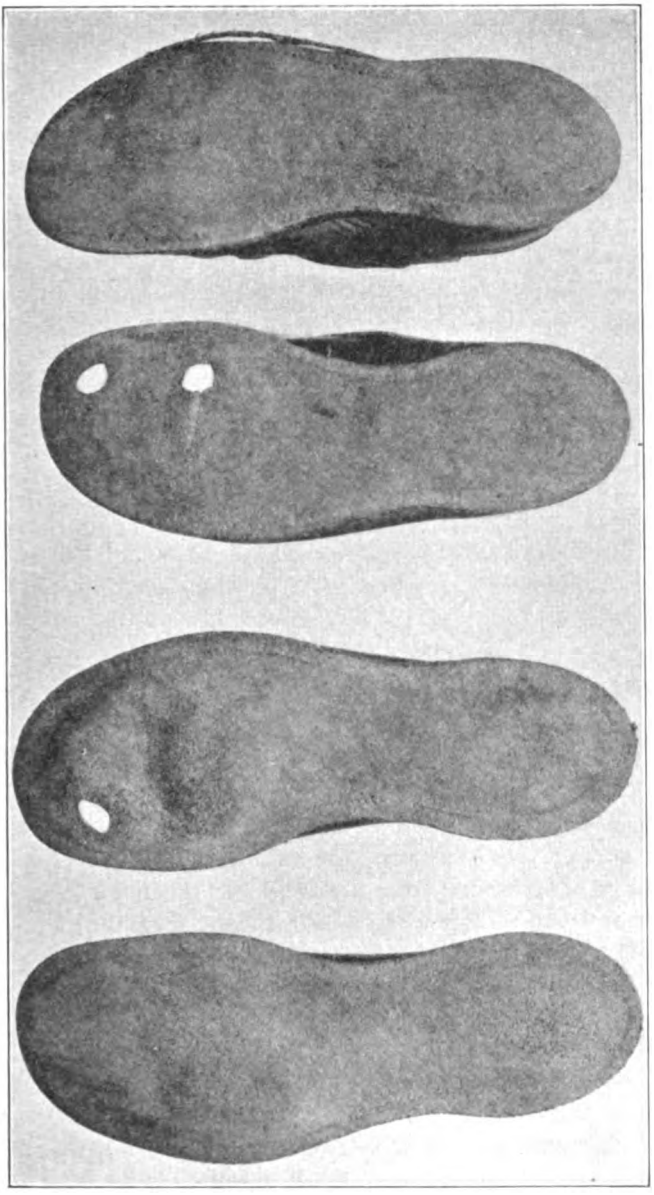

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FIG. 2.

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Individual results in these experiments are often exactly contradictory, owing to the effect of one or more of the above mentioned causes, and it is therefore possible to draw conclusions only from the averages on a large number of soles.

The results given in the following table were obtained by first determining the total thickness worn away during a recorded number of hours' wear, and then calculating this to the thickness which would be worn away if the leather had worn at the same rate for 1,000 hours, which would represent approximately 3 months' wear. The results thus obtained were grouped according to the section of the hide from which the soles were cut and averages made for these groups.

TABLE I.—RESULTS OF ACTUAL WEARING TESTS OF SOLE LEATHER FROM DIFFERENT PARTS OF THE HIDE.

(Expressed as inches worn off in 1000 hours' wear.)

	Maximum wear inches	Minimum wear inch	Average wear inch
Butt (7 leathers)	0.597	0.402	0.464
Heads (2 leathers)	0.515	0.508	0.512
Shoulders (8 leathers)	0.712	0.494	0.605
Belly (4 leathers)	1.110	0.787	0.944

These average results substantiate the belief which has been generally held for many years that the best wearing sole leather comes from the butt of the hide, and that the shoulder, and especially the belly, are much less resistant to wear than is the butt. It is also interesting to note that the leather from bull heads gave results equal to, if not better than, those obtained with shoulder leather. Leather from the butt wore on the average at least twice as long as that from the belly portion of the hide, and about one and one-third times as long as that from the shoulder portion. In every case the results from the three sections gave the same relative order of wear as indicated by the average results.

As previously stated, these results are but preliminary. A series of experiments upon a wear-testing machine developed by this laboratory is nearing completion. It is planned in the near future to start extensive field service wearing tests which are to be co-ordinated with mechanical wearing tests.

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THE LYOTROPE SERIES AND THE THEORY OF TANNING.*

By Hugh Garner Bennett, M. Sc.

The past year (1917) has witnessed a revival of interest in the theory of tanning, but has produced little sign of general agreement. The recent contributions of Procter, of Moeller, and of Wilson exhibit still a striking divergence of view. Thus Wilson[1] regards vegetable tannage as a simple ionic reaction and writes it thus:

$$R\begin{cases} NH_2^+ \\ | \\ CO \end{cases} + (\text{tannate ion})' \rightleftharpoons R\begin{cases} NH_2\ (\text{tannate}) \\ | \\ CO\ (\text{vegetable-tanned leather}) \end{cases}$$

and the chrome tannage as a simple but slow chemical reaction, thus:

$$3\,R\begin{cases} NH \\ | \\ CO \end{cases} + Cr(OH)_3 \rightleftharpoons (NH_2.\ R.\ COO)_3\ Cr.$$

On the other hand, Moeller[2] states that "the changes which the tannin colloids undergo after being taken up by the hide substance were found to depend solely on irreversible colloidal changes of state. *Simple chemical processes do not occur.*"

With such divergence of opinion existing, the writer ventures to offer his own views upon this question, and to echo Mr. Wilson's statement that "general discussion and criticism, if given with the sole purpose of approaching nearer to the absolute truth, would undoubtedly prove of immense value."

PART I.

The Lyotrope Series.

Recent investigations have shown that the essential physical properties of water are affected by dissolved substances in a definite manner and to a fixed extent, and that these substances exhibit a sequence in order of their effect. This sequence is also exhibited in the essential properties of water as solvent and as dispersion medium for colloid sols. The sequence is known as the "lyotrope series." Thus the numerical value of the com-

* *J. S. L. T. C.*, Nov. and Dec., 1917.

[1] *Collegium* (London), 1917, pp. 109-110.

[2] *Collegium* (London), 1917, p. 39.

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pressibility of aqueous solutions is reduced below that of water by salts which, with the same kation, exhibit an effect in the following order: $CO_3 > SO_4 > Cl > Br > NO_3 > I$. This same order is observed in the effect on the values for the surface tension, density and viscosity of these solutions. On the other hand, the kations have a similar sequence of effects, $Mg < NH_4 < Li < K < Na < Rb < Cs$, which appears when salts of the same anion are chosen. It is not surprising to find that this lyotrope series exhibit an analogous influence on the chemical reactions of water, *e. g.*, the hydrolysis of esters. In the hydrolysis by acids SO_4 retards the action, the other anions and the kations accelerate it in the lyotrope order. In the hydrolysis by bases the series is reversed. Similarly, the lyotrope series exert the same order of effect upon the inversion of cane sugar and other reactions.

This lyotrope influence has also been shown to exert considerable effect in the behavior of lyophile sols. A hydrosol may be a two-phase system in which the disperse phase is solid or liquid (suspensoid or emulsoid); but it is now recognized that emulsoid sols have usually another characteristic, *viz.*, a marked affinity between the two phases; hence it is now more usual to classify sols into "lyophobe" and "lyophile." With the lyophobe sols (broadly speaking, the suspensoids) the addition of foreign substances apparently affects the disperse phase only, but with the lyophile sols the effect on the dispersion medium is also important, and may overshadow the other. Now in hide gels and tanning sols we are dealing with lyophile systems, and there are many points of behavior in which lyotrope influences become prominent. Similar effects are observed upon other lyophile sols (*e. g.*, albumin, agar-agar, etc.), which differ widely in chemical nature. Thus the salting out of albumin (reversible precipitation) is influenced by sodium salts in lyotropic sequence as follows: The anions hinder precipitation. In order of precipitating power they are:

$$\text{citrate} > \text{tartrate} > SO_4 > \text{acetate} > Cl > NO_3 > ClO_3 > I > CNS.$$

The sulphates illustrate the kation effect, which is independent and which favors precipitation:

$$Li > K > Na > NH_4 > Mg.$$

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If the experiments be carried out in faintly acid solution this order of effect is exactly reversed, iodide and cyanate having the greatest effect and citrates the least. The coagulation temperature of albumin and the coagulation by other organic substances is similarly influenced by the lyotrope series.

Lyotrope influence also exerts a powerful effect on the behavior of gelatin sols and gels. The gelation temperature is influenced thus:

raised by $SO_4 >$ citrate $>$ tartrate $>$ acetate
lowered by $Cl < ClO_3 < NO_3 < Br < I$.

The kation effect (small) is $Na > K > NH_4 > Mg$.

Other lyotrope substances raise or lower the temperature thus:

glucose $>$ glycerol $-$ (H_2O) $-$ alcohol $<$ urea.

The effect on gelation is also illustrated by the change of viscosity of the sol with time. The same lyotrope order is found.

In the salting out or precipitating of gelatin with salts the order of anions is lyotrope.

$SO_4 >$ citrate $>$ tartrate $>$ acetate $> Cl$.

Also the osmotic pressure of gelatin sols is markedly lowered by neutral electrolytes in lyotrope sequence.

$Cl > SO_4 > NO_3 > Br > I > CNS$.

Similarly lyotrope influences are shown in the modulus of elasticity: substances which favor gelation increase elasticity, while substances which favor solation decrease elasticity. The order is again lyotrope.

The permeability of the gel is affected by lyotrope influences; alcohol and glycerol reduce diffusion through gelatin (or agar), and urea, chloride, and iodide increase it. (Similarly, the diffusion of sols through "semipermeable" membranes is affected by lyotrope influence.) The lyotrope series also influence the optical activity of gelatin sols and the double refraction of strained gels.

The swelling of gelatin (and other gels) is very strongly influenced by the lyotrope substances, and merits more attention than it has received. Hence this lyotrope influence exerts a profound effect in leather manufacture, and explains many known facts in liming, deliming, and tanning. It is one of the main objects of this paper to insist upon the importance of this lyotrope

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influence and to point out its primary importance in any satisfactory theory of tanning. The swelling of gelatin is favored by the substances which reduce the modulus of elasticity; it is hindered by the substances which increase elasticity. Hence there is also a close connection with the effect on gelation: what favors gelation hinders swelling; what hinders gelation favors swelling.

$$SO_4 > \text{tartrate} > \text{citrate} > \text{acetate} > \text{alcohol} > \text{glucose} > \text{cane sugar} : — (\text{water}) < Cl < ClO_3 < NO_3 < Br < I < CNS < \text{urea}.$$

The substances before water hinder imbibition, those after it favor it. The effect is additive: appropriate concentrations of different salt leave the gelation temperature and imbibition unchanged.

This lyotrope influence has in tanning a double effect; a strong effect on the imbibition of the hide gel and an effect less marked on the gelation or diffusion of the tannin sol. These effects are always present in the tanning process and exert an almost predominant effect upon the quality of the leather produced, the rate of tannage, the "weight" produced, the color, the quality of the grain, etc., etc. Before entering into this complex question it will be perhaps advantageous to take illustrations from familiar and simpler problems. The analysis of tanning materials affords many such illustrations, and lyotrope influence explains many long standing anomalies. In detannization we have a partly swollen gel (hide powder) immersed in an infusion which contains lyotrope substances. These affect the swelling of the powder. It has recently been pointed out by the writer that this swelling of the hide powder has a predominant influence on the results obtained. (*Collegium*, 1917, p. 85.) Tannin is always adsorbed with practical completeness, but the astringent non-tans, of which gallic acid and catechin are types, are adsorbed very incompletely, the determining factor being the active surface of hide powder. This active surface is subject to lyotrope influence, which, therefore, is a prominent cause of variations in non-tan determinations. Thus the neutralization of hide powder before chroming forms sodium salts of organic acids, which reduce imbibition, and decrease the active surface of the powder. Hence a greatly lessened adsorptions of non-tans occurs and a higher percentage of non-tans is recorded. (*Collegium* (London),

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1917, p. 85.) Parker and Bennett (*J. S. C. I.*, 1906, p. 1193) investigated the effect of adding various non-tanning substances to the liquor in which tannin was being estimated. The results have always been somewhat puzzling until the explanation became apparent to the writer as lyotrope influence. On adding glucose and magnesium sulphate to gallotannic acid it was found that the amount of tan estimates by the "shake method" was decreased. These are substances which hinder imbibition. In analysis they reduce the swelling of and active surface of the hide powder and result in a lessened adsorption of astringent non-tans and higher non-tan residues. Dr. Schell has recently had a confirmatory experience (*La Halle aux Cuirs*, Aug. 12, 1917, and *J. S. L. T. C.*, 1917, pp. 73 and 87). He found that the permanent hardness of Paris water was sufficient to cause an appreciable effect in this sense. He was surprised, but the lyotrope influence affords a ready explanation. It is noteworthy that common salt (NaCl) was found by Parker and Bennett to cause a slight increase in the tannin estimated, but a slight decrease with stronger solutions. This is in harmony with the general effect of NaCl on the imbibition of gels. It is clear that the addition of such substances (*e. g.*, K_2SO_4 or cane sugar) to the tannin infusion would cause the present official method to give more correct results in tan. The writer is not inclined to propose this remedy for the adsorption of non-tans, as he considers his alternative proposals (*J. S. C. I.*, 1914, p. 1182, and *Collegium* (London), 1917, p. 94) to be better: it would be of no service to use lyotrope substances in addition to these proposals as more hide powder would be needed for effective detannization.

It is interesting to note that those materials which contain much sugar in the non-tans are more correctly estimated in the official method on account of this lyotrope influence of sugar. Thus myrobalans, valonia, and sumac have *relatively* more tannin than mimosa bark, gambier, and quebracho than is shown by the official analysis. In other words, the percentage of tannin in the catechol tans is much over-estimated by the official method. This is more especially true when much adsorbable non-tan is associated (*e. g.*, gambier). Be it far from the writer to suggest the adulteration of tanning extracts, but it follows from the above that if the appropriate lyotrope substance be added (say urea) the hide powder will swell and the analysis will

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show a large apparent tannin content. This case of tannin analysis has been discussed at length, not only because it is interesting and commercially important, but also because it is typical of the influences at work in the earliest stages of tanning. The circumstances are quite similar and analogous; an excess of hide gel is immersed in a liquor containing little or no tan but relatively large quantities of (1) astringent non-tans (colloid sols), and (2) lyotrope substances such as glucose, acetates, lactates, etc., of lime and soda, sulphite of soda, etc. These last tend to hinder imbibition, just as in analysis, and consequently reduce the active surface and consequent adsorption of gallic acid, catechin, etc. Neutral substances exhibiting a lyotrope influence which favors imbibition may also exist in the early tan liquors, but they are less common. When in very dilute solution sodium chloride falls into this class, but its effect is always slight and is reversed with increased concentration. Possibly hide degradation products of the urea type may be present and exert some influence, but the predominant lyotrope influence of old tan liquors is against imbibition. This lyotrope hindrance to plumping is one of the main factors in producing "mellowness" in old tan liquors. The effect of such substances is (1) to cause a lessened adsorption of tannin, owing to the decreased specific surface of the hide gel; (2) to produce a lessened adsorption of non-tans for the same reason, but to a relatively greater extent; (3) to cause a tannage of the hide fibers in an unswollen condition, and therefore to produce a soft leather; (4) to cause a "leathering effect" of its own by the abstraction[3] of water from the fibers. All these effects are due to lyotrope influence *on imbibition*.

There is also the lyotrope influence on diffusion to be considered. The effects just previously discussed are concerned only with changes in swelling and in adsorption before any penetration of the tanning sol into the hide gel takes place, but there is also the effect of the lyotrope series on the penetration of the hide fiber itself. This penetration should be carefully distinguished from the penetration of the hide which merely involves diffusion through the solution surrounding the hide and its fibers. A hide may be "struck through," but the hide gel may be little

[3] Dehydration is a rather unsuitable term, inasmuch as there are no definite hydrates.

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penetrated, if at all. The diffusion of the tanning sol into the hide fiber gel is subject to a lyotrope influence of great complexity. In the first place, diffusion into the gel is hindered by the citrate end of the lyotrope series and encouraged by the urea end of the series. A mixture of lyotrope substances produces an effect according to the predominant influence. In the case of old tan liquors, as we have seen, the effect is usually that of the citrate end,—*i. e.*, old tan liquors hinder diffusion into the gel. In the second place, however, we have to consider also the lyotrope influence on the powers of diffusion of the tannins and colloidal non-tans. This effect is also mixed, but usually tends to increase the powers of diffusion of the sol through membranes. Many sols diffuse rapidly when thus influenced, but, though lyotrope influence be at work, it is perhaps a question whether this is the only factor in operation. Usually, however, the lyotrope influence of an old tan liquor will favor the increased diffusion of the tanning sol. The total effect, therefore, on the diffusion of tanning sols into hide gels is very complex. The diffusive power of the sol is enhanced, but the gel's power of resistance to diffusion is also enhanced; which becomes predominant will depend upon other factors. One of the most important results of this complex lyotrope influence will be the *relative* total effect of the diffusion of the tannins compared with that of the colloidal non-tans. This, obviously, will influence largely the quality of the leather, but on this point we are still much in the dark and experiment is somewhat difficult. The total effect on diffusion is further complicated not only by the lyotrope influence on imbibition, discussed above, but by the extent to which this has been combatted by swelling with acids. These influences also cause changes and differences in the relative diffusion of tanning sols, as well as in the absolute powers of diffusion.

Another lyotrope influence in tanning remains to be discussed, *viz.*, the influence on gelation. Both collagen and the tanning sols are lyophile colloids which exhibit great increase of viscosity on the abstraction of water, culminating in the formation of a gel. In tanning we have already the hide in gel form, so that we are now concerned chiefly with the tanning sols. It is the writer's opinion that the gelation of these sols is a fundamental action in the tanning process. From this point of view, the object of tanning is to produce the gelation of the tanning sol on

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the hide fibers. If any adsorbent be immersed in an emulsoid sol, the resulting adsorption involves essentially, not a precipitation, reaction, decomposition, or a deposition of solid, but merely a change in the concentration of the sol, generally (positive adsorption) an increase in the concentration of the surface layer. Now in tanning this increase in concentration of the tanning sol at the interface of sol and gel is, in effect, the first stage in the gelation of the tanning sol. The gradual transfer of the hide to more concentrated sols ("stronger liquors") produces a still greater concentration at the interface, being in effect a continued gelation of the tanning sol on the fiber surface. Modern tanners often employ viscous liquors of 120°–130° B. to finish the tanning process. However great the viscosity in the volume concentration, it is certainly greater in the surface concentration. Modern methods of weighing by "extract-vatting," by dusting down the leather in pile with powdered solid extracts represent the next stage in producing the gelation of tanning sols in the leather, and this is completed by drying out the leather in the sheds. That the gelation of tanning sols is a fundamental action in tanning seems beyond dispute; the primary adsorption, the gradual tannage, the weighting, and the final drying of the leather are all concentration of the lyophile sol on the fiber surface, and such a concentration of lyophile sol is gelation. It is not suggested that this is either the only or the essential action of tanning, but it is insisted that this is one of the prominent and essential actions. Adsorption by and diffusion into the gel (as mentioned above) and mutual precipitation (as discussed below) have also their place in the tanning theory, to a relative degree varying with every tannage, and indeed with every sample of leather. Now gelation is one of those colloid phenomena which is distinctly influenced by the lyotrope series, and what it is wished to emphasize here is that the gelation of the tanning sols upon the hide fiber must be influenced by the presence of lyotrope substances. These will, in all probability, have a different relative effect upon the individual tannins and colloidal non-tans, and consequently be of considerable importance in determining the quality and weight of leather produced.

It should be noted that the lyotrope influence is general, and is found in most if not all tannages, but especially in the vegetable and mineral tannages. It is important in vegetable tan-

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nage, even more prominent in chrome tannage, and yet more so in the alum tannages.

PART II.

The preceding discussion of lyotrope influence was undertaken partly to emphasize the importance of a neglected factor in tanning, and partly to facilitate the statement of the author's opinions on the theory of tanning, which statement will now be attempted.

The author pins his faith to the adsorption theory. This may perhaps have become already obvious in the discussion of Part I. The hide gel is an adsorbent presenting an enormous specific surface. This is partly due to its gel nature, but also partly to its fibrous structure. Like all gels it is a strong adsorbent. Tanning liquors on the other hand are emulsoid sols, and like all lyophile sols they are exceedingly liable to be adsorbed. In the immersion of a hide gel in a tanning sol, we have therefore the ideal conditions for a very decided adsorption. The first essential action of the tanning process is therefore, the production of an adsorption equilibrium. This view has been widely accepted since about 1908, and has been confirmed by the experimental work of Von Schröeder, Stiasny, and others. This adsorption is essentially an inequality of concentration in the tanning sol. It is due to considerations of surface tension and surface energy, and exists before the immersion of the pelt. The surface concentration being greater than the volume concentration, any considerable extension of surface in a fixed volume of sol must produce a considerable decrease in the volume concentration. This occurs when the hide gel is inserted in the tanning sol. The amount adsorbed is proportional to the extension of surface, and is therefore a function of the specific surface of the adsorbent. Hence the specific surface of the hide gel is one of the most important factors in the tanning process. This is subject to much variation with consequent variations in the nature and quality of the resulting leather. These variations of specific surface are due to many causes among which may be mentioned: (1) the natural compactness or openness of texture of the hide gel; (2) the extent to which the fibers have been split into constituent fibrils by the plumping of liming; (3) the extent to which the interfibrillar substance has been dissolved during liming and

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bating ; (4) the swelling in liquor due to the free acids, naturally present or artificially added ; (5) lyotrope influence of neutral salts and organic substances as discussed in Part I. All these, and probably other factors influence the specific surface of the gel, and consequent extent of adsorption. The amount of adsorption, on the other hand, naturally is also dependent on the exact nature of the colloid tanning sol. In the case of vegetable tannage a complex mixture of substances exists in the sol and the resulting adsorption is also therefore complex.

Adsorption, however, involves no penetration of the gel, but merely a redistribution of concentration in the sol. Diffusion into the gel is the second essential action in the tanning process. The extent of this diffusion is determined by the powers of diffusion of the sol, and by the power of resistance to diffusion possessed by the gel. The lyotrope influence which enhances or reduces both these powers simultaneously though possibly to a different degree has already been discussed (Part I.) In vegetable tannage the colloids of the tanning sol are a complex mixture with widely differing powers of diffusion. They are broadly classified into three types: (1) the so-called "astringent tans" which possess the least powers of diffusion ; (2) the so-called "mellow tans" with greater diffusive powers and, (3) the colloidal non-tans, of which gallic acid and catechin are typical examples possessing still greater diffusive powers. It is now recognized that even colloids diffuse, the difference being one of degree. Generally speaking an increase of imbibition of the gel assists the diffusion of all substances.

The adsorbed tanning sol has the option of diffusing into the gel or of stopping in the outside of it. Though the difference is perhaps one of degree, it is necessary to consider the alternative. If a tanning sol does not diffuse, its concentration at the fiber surface continues to increase, especially in those methods when the gels are continually moved into stronger sols. This involves the gradual gelation of the lyophile sol at the interface of sol and hide fiber. This gelation is subject to lyotrope influence as discussed in Part I., and is another essential action in the tanning process.

Thus far, we find tanning to consist of adsorption followed by either diffusion into the gel or gelation at the interface, but gen-

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erally both. We have now to consider another essential action of tanning, *viz.*, the mutual precipitation of oppositely charged colloids. It is a feature of the colloid state of matter that the disperse phase is electrically charged to some extent. The charge may be + or — and may be large or small. The sols exhibit electrical conductivity and migration occurs in the direction determined by the nature of the charge. Oppositely charged sols precipitate one another, the precipitate containing both colloids. The maximum precipitation occurs when the + charge of one sol exactly neutralizes the — charge of the other. There is thus an electrical equivalence, an amount of one sol which is equivalent to a given amount of another. This mutual precipitation is exhibited both by lyophobe and by lyophile sols; though there are striking differences. In the case of precipitation by electrolytes the "valency rule," is the determining factor, *viz.*, that precipitation is mainly effected by the ions of opposite charge, and that the precipitation-concentration is a function of the valency of these ions. There is also an independent stabilizing influence due to the ion of opposite charge, less powerful, but also following the valency rule. This important generalization holds also in the influence on other electrical properties of the sols, *e.g.*, electroendosmosis and cataphoresis. The potential difference between the two phases of a sol may be increased or decreased by addition of other substances to the dispersion medium. Indeed the potential difference may be diminished until it is finally reversed in sign, with a corresponding change in the electrical behavior. The effect of acids and alkalies is exceedingly strong in this sense. The presence of salts also effects such a change and follows the valency rule, *i.e.*, in a negative sol the valency of the kation is the predominant factor. In the case of lyophile sols there is strong evidence that the nature of the charge is in many cases largely an accidental matter, being determined by the medium in which it happens to be, their normal condition being electrical neutrality. Thus gelatine in the presence of acid is a positive sol and in the presence of alkali a negative sol. The predominant effect of acids and alkalies is regarded as due to the predominant influence of the hydrion ($H^{\cdot}$) over all other kations, and to the similar predominance of the hydroxyl ion (OH') over all other anions. All hydrosols contain $H^{\cdot}$ and OH' ions, the sol is positive or negative, according as the

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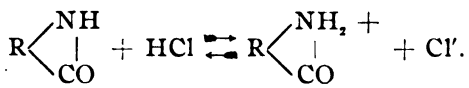
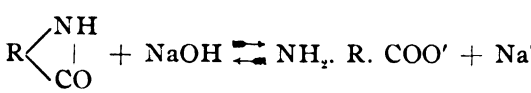
disperse phase receives the H· or the OH′ ion. The writer purposely chose "receives" as a non-committal word, for on its interpretation hangs the theory of the origin of the electric charge. This "reception" of the H· and OH′ ions has been variously ascribed to their solubility in, their diffusion into, their adsorption by, and their chemical combination with the colloid. There is here room for much difference in opinion and still more room for experiment. Many explanations have been made to fit the facts, but that does not make them correct. As the writer is stating here his own views he has got to come "off the fence" and favor one of these theories rather than the others. It seems to him that the issue lies mainly between the chemical combination and the adsorption theory, for little is known of the solubility or diffusibility of ions. In this connection reference must be made to the work and views of Procter and his collaborators, who have advanced the theory of chemical combination with great force and used their generalization to explain the swelling and falling of colloid jellies, and to account also for the electric charge [see *Collegium* (London), 1917, p. 3, for bibliography and summary]. These authors explain the action of acids on gelatin and collagen as due to a chemical combination of the acid with the gelatin, with the formation of a highly ionizable protein salt, *e.g.* gelatine chloride, thus:



The osmotic pressure of the anion causes swelling, and the positive charge of the acid cation is thus communicated to the colloid by its inclusion in the imide group. In alkaline solution the proteid also is said to form a similar highly ionizable salt but with the carboxyl groupings of the proteid molecule. Thus with caustic soda:



On these assumptions Procter accounts well for the swelling effect of acids and alkalies, and for the appropriate electric charge on the protein in acid or alkaline medium. The theory thus depends upon the amphoteric character of collagen and

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other proteids. The amount of hydrion (or anion) "received"

$$z = \sqrt{4ex + e^2}$$

is on this theory given by the expression where z = amount of ion taken up, x the concentration of the surrounding solution, and e the excess conçentration of the diffusible ions in the jelly over that in the surrounding solution. One feels that the work of Prof. Procter on this big subject is as yet uncompleted, and one looks forward to further developments of his theory and to its more perfect correlation with the wider facts of colloid chemistry, especially with the swelling and falling of jellies which contain no amido or carboxyl groups and with the lyotrope influence on imbibition. Equally does one look forward to his criticism of alternative theories as to the origin of the electric charge, especially of the adsorption theory. In the meantime his extensive work on, and prolonged consideration of this subject contribute to the conclusion that his theory should receive most respectful consideration.

Prof. Procter's disciple, Mr. J. A. Wilson, has energetically drawn certain corollaries from Procter's theory which are very provocative of criticism. These have been elaborated into a theory of tanning which the writer has a strong disinclination to accept. In vegetable tannage the gelatine ion is said to react with the ionized tannic acids with the production of an insoluble precipitate which is leather. The chrome tannage is of fundamentally different nature, and the chrome combines with the acid groups of the protein molecule after hydrolysis of the —NH—CO—groups. Mr. Wilson's equations have been quoted in the introduction to this article. He has definitely recognized (*J. A. L. C. A.*, 1917, p. 122), that the chemical combination—ionization theory is in disagreement with the adsorption theory as to the origin of the electric charge on the gelatin particles and also in regard to its quantity, the two equations being :—

Ionization theory	*Adsorption theory*
$z = \sqrt{4ex + e^2}$.	$z = k \sqrt[n]{x}$.

He adopts the ionization theory as resting on "well founded assumptions," and lightly dismisses the adsorption theory as "merely empirical."

It is perhaps typical of Mr. Wilson that he prefers to theorize

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by the deductive rather than by the inductive method. He builds his theory of tanning on Procter's theory of imbibition, which rests upon the ionization theory. It is perhaps equally typical of the writer that he prefers the inductive method, and would prefer to build his theory of tanning as much as possible upon experimental facts rather than upon other theories. In the realm of science the author must confess himself a thorough pragmatist, and Wilson's airy dismissal of the adsorption theory as empirical is sufficient to induce the writer to defend it. That the adsorption theory had an empirical origin is, in the writer's opinion, one of its strongest recommendations. That adsorption is a widely distributed phenomenon is another strong recommendation. Moreover, the adsorption law is not "merely empirical;" whatever its origin, it now rests upon as sound a basis of theory as the ionization theory. The adsorption law is almost a necessary deduction from surface tension phenomena and rests upon equally "well founded assumptions." The author will not now attempt any further criticism of Wilson's theory of tanning, except definitely to state that he is in profound disagreement with Wilson's conclusions: (1) that vegetable tannage is an ionic reaction, and (2) that chrome tannage is fundamentally different in action and nature from vegetable tannage. Meanwhile the author is content to adopt the adsorption theory and will now proceed with his own views as to the nature of the tanning process.

The adsorption theory explains the origin of the electric charge on colloid particles as an adsorption of the electrically charged ions, and experimental investigations of the electrical properties show that the effect of ions on the electrical properties is greatest at very small concentrations, rapidly falling off as the concentration increases. The fact that the effect of ions is relatively greatest at small concentrations is what is expected from the adsorption law. The adsorption theory explains the predominant effect of hydrion and hydroxyl ion on the electric charge and electrical properties by stating that these ions are more readily adsorbed than other ions. Further, it concludes that OH' is more readily adsorbed than $H^{\cdot}$, for most sols are negative to water. In the case of many lyophile sols the nature of the charge is often an accidental matter, and the pure colloid is iso-electric with water. The addition of acid or alkali to such

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a sol makes it positive or negative by the relatively greater adsorption of $H^{\cdot}$ or OH' ions respectively. Collagen and gelatin are primarily slightly positive, but the electric charge is easily reversed and is practically determined by the acidity or alkalinity of the medium. In tanning the medium is invariably acid so that collagen is a positive gel.

Aqueous infusions of vegetable tanning materials yield a sol which is lyophile, and which, like most sols, is negative. Most lyophile sols are a stage nearer true solutions than the lyophobe, and the hydrophile sols of the tannins are in all probability nearer than the average of their class. Indeed they verge into what have been called "emulsides," *i. e.* substances intermediate between emulsoids and true solutions, colloid sols having unusually high dispersity (amicrons). Now a hydrophile sol is conceived as having the colloid as well as the dispersion medium in both phases; hence the dispersion medium of a tannin sol contains some tannin in true solution, and in this solution the tannin ionizes to some extent giving the hydrion and an organic anion. It is important to visualize correctly the constitution of a tannin infusion, in order to understand its properties and behavior. It consists then of minute droplets (less than 6 $\mu\mu$ diameter) of a strong solution of tannin dispersed in a much more dilute solution of tannin. The droplets adsorb OH' from the ionization of the water forming negatively charged particles, while some of the tannin dissolved in the dilute solution is ionized. The disperse phase will of course tend to adsorb the ions of the dispersion medium, and although the charges are equal and opposite, the hydrion is the more strangely adsorbed and tends to discharge the negative charge on the disperse phase. It is clear that the addition of acids, (especially if strongly ionized) to the dispersion medium, will also tend to discharge the adsorbed hydroxyl and precipitate the colloid. Thus in strong tan liquors a precipitate is obtained with numerous acids, and the text books record that tannin is "insoluble in dilute sulphuric acid." This indeed is one of the main functions of the acids in tan liquors, to render the sol less negative and more liable to precipitation. Hence sour tan liquors give a quick tannage of the exterior of the hide, exhibit relatively less diffusion into the hide, but give a heavier precipitation. The negative sol, nearly precipitated by the acids, is immediately

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precipitated by the positive gel. Conversely, sweet liquors tend to diffuse more quickly through the hide and through the hide fibers, but give a lighter tannage. The addition of alkali to tan liquors has of course opposite effects. The alkali tends to stabilize the negative sol. In practice alkali is added only when a limed hide is inserted in a much used and acid liquor. The lime, soda, and ammonia then neutralize a portion of the acids of the liquor, forming lactates, acetates, etc. In this case, however, not only is the tannin stabilized by the neutralization of the hydrions, but there is also a new effect, that of the ions of the neutral salts. The presence of neutral salts in tan liquors has therefore an effect on the tanning process second only in importance to the hydrion concentration. This influence is in accordance with the valency rule, the ions tending to stabilize or precipitate the tan according to the quantity and nature of their own charge. As the sol is negative the kations have predominant influence in tending to precipitate the colloid; thus $Fe^{\bullet\bullet\bullet} > Ca^{\bullet\bullet} > Na^{\bullet}$. Hence the danger of "iron stains" and "lime scum." The anions tend to stabilize the tan, especially if multivalent; thus $PO_4''' > SO_4'' > Cl'$. Now organic anions are particularly liable to adsorption, and as these frequently exist in such liquors their effect is of distinct importance in the tanning process. They also of course obey the valency rule; thus citrates$''' >$ tartrates$'' >$ acetates$'$. The presence of such salts as these, which stabilize the negative sol, especially if combined with a monacid base, will favor the diffusion of the tan, instead of its early precipitation. Hence, if even the most astringent tans be used, they may be "mellowed" by the addition of such salts to the liquors. The hide is quickly "struck through" and a soft leather results, partly also on account of the lyotrope influence in reducing imbibition, as discussed above. This is doubtless the explanation of some experiments published by the author some years ago (*J. S. C. I.*, 1908, p. 1193) in which substances like sodium sulphite, and sodium acetate were added to mimosa bark liquors. In many tanning infusions, such salts occur naturally. We see, therefore, that salts of the "sodium citrate" type tend most to stabilize the tanning sol, and assist diffusion both through the hide and into the gel, and that salts of the "aluminum chloride" type tend most to precipitate the tan. In general, the salts usually present in used tan

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liquors tend to stabilize the sol and prevent immediate precipitation. This is another factor, producing what is known as the "Mellowness" of old liquors. It should be remembered, however, that vegetable tan liquors are mixtures of sols of differing nature, charge and dispersity and that the different individual colloids are affected in perhaps different degrees.

Thus far we have considered only the effect of electrolytes in determining the nature and amount of charge on the hide gel and on the tanning sol. We have now to consider the action of the one on the other, the mutual precipitation of the two colloids. Now there is clearly an amount of negative tanning sol which is equivalent to a given amount of positive hide gel, amounts which possess equal and opposite charges and which disappear in the electrical discharge associated with the co-precipitation of oppositely charged colloids. It must be emphasized, however, in contradistinction to Wilson, that this is not a chemical equivalence, nor is the precipitate,—which must contain the two colloids in *practically* constant proportions—to be regarded as a chemical compound, in spite of its nearly constant composition. *The equivalence is electrical*, and the maximum precipitation occurs when the positive charge on the one sol *exactly* equalizes and neutralizes the negative charge of the other. With lyophile colloids, moreover, there is a further complication known as "protection," the essential feature of which is that an excess of either positive or negative sol "protects" both from precipitation. The co-precipitation and electrical discharge occur only in a middle zone—usually narrow, and flanked on either side by zones of partial precipitation. On either side of the optimum mixture the mixed sol is negative or positive according as one or other component is in excess, although the sol contains both; and this is true whether partial precipitation has taken place or not. The mutual precipitation of positive hide gel and negative tanning sol is, therefore, very far removed from a simple ionic reaction and the precipitate cannot be called a chemical compound. The precipitate from these has not indeed a constant composition; it contains certainly both components, *but so does the remaining sol*, except in those rare circumstances where absolutely complete precipitation has occurred. In tanning, precipitation is always on one or other side of the optimum, and the precipitate does not contain the

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whole of the component which is in defect.[1] Thus the idea of "soluble leather," suggested by Dr. Parker, has a sound theoretical basis.

As we are thus not dealing with an ionic reaction it is a matter of first importance in tanning to consider those factors which affect the optimum precipitation, for these naturally also determine the "completeness" or "soundness" of the tannage. Four of these factors of special prominence and importance will be mentioned. The optimum precipitation is affected: (1) by the number of particles required, or, in other words, by the amount of electric charge on each particle. This (as mentioned above), is determined by (*a*) the hydrion concentration, in a less degree by (*b*) the concentration and multivalency of other kations, and in a still less degree but in the opposite sense by (*c*) the concentration and multivalency of the anions, especially the strongly adsorbed organic anions; (2) by the size of the particles, *i. e.*, the dispersity of the sol: hence, different tanning materials must give different weights; (3) by the *relative* concentration of the two colloids: in practice this involves chiefly the concentration of the tanning sol, *i. e.*, a weak liquor takes longer time to attain precipitation; and (4) by the rate of admixture of the two components: it is a general occurrence in colloid precipitations that if the precipitating reagent be added slowly a much larger amount is needed for complete precipitation, the slower the reagent is added the greater is the excess of it needed. Thus the hide gel in tan liquors becomes "acclimatized" to the tanning sol, and the more slowly the hides are moved forward into stronger liquors, the more tannin is eventually needed. This is one of the theoretical justifications of the time-honored method of tanning in liquors of increasing strength.

* * * *

The preceding remarks have been all primarily applicable to the ordinary vegetable tannage, and it is now necessary to answer the theory of chrome tannage in relation to the above. How far does the chrome tannage offer analogies to the theory of vegetable tanning just outlined? Wilson regards the chrome tannage as something fundamentally different in essential nature,

[1] Hence the unsatisfactoriness of removing tannin from solutions by adding a gelatin solution.

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but the writer would suggest rather that those essential actions of vegetable tannage assigned above, are also essentially found in the chrome tannage, the difference being mainly one of degree. Thus the hide gel is immersed into a lyophile sol,—the chrome liquor—and there follows lyotrope influence, adsorption, gelation of the tanning sol, as well as diffusion into the gel, and finally also, probably, precipitation of the tanning sol at this interface.

In chrome tannage the lyotrope influence is much more prominent than in *vegetable* tannage, but the effect is in the same sense, *viz.*, to reduce the imbibition of the hide gel. Thus the potassium sulphate in a chrome alum liquor has its own specific action of this kind and contributes to the leather formation. Unhydrolyzed chromium sulphate, and the sodium sulphate formed in "making basic," act also in the same sense.

The tanning sol is probably chromium hydrate, formed by the hydrolysis of chromium sulphate: it is a lyophile or emulsoid sol and is in consequence very strongly adsorbed by the hide gel. This adsorption, involving a concentration of lyophile sol, is the first stage in gelation, which occupies a relatively more prominent place in the chrome than in the vegetable tannage. Some diffusion into the gel also occurs, and both the gelation and diffusion of the sol are affected by lyotrope influence, but to a greater extent than in the vegetable tannage. Thus far the analogy is almost complete.

There remains the question of the precipitation of the tanning colloid at the interface. This is a point which has not yet been thoroughly investigated, and which offers considerable difficulty to a clear understanding, but the matter may be probably summarized thus: the adsorbed chromium hydrate is precipitated at the interface of gel and sol to some extent, chiefly through the neutralization of its charge by the oppositely charged ions of the electrolytes present, but possibly also—in the last stages of manufacture by the mutual precipitation of oppositely charged gel and sol.

To illustrate the matter, the case of a basic chrome alum liquor will be considered. The chromium hydrate sol is primarily a positive sol, just like ferric and aluminium hydrate sols: *i. e.*, in water they are somewhat exceptional, in that they adsorb $H^{\cdot}$ rather than OH'. To cause precipitation, therefore, it is neces-

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sary to make the sol less positive and more negative. The positive charge of the sol, however, is greater than in water, because of the free acid formed in the hydrolysis, which results in the adsorption of more hydrions by the sol. Hence to insure precipitation steps must be taken to reduce the adsorption of hydrions by the chromium hydrate sol. In practice such steps are taken, and to such an extent that there can be little doubt that the chrome sol is not far from its isoelectric point. Among these "steps" are (1) making the liquor "basic"—*i. e.*, adding alkali to neutralize much of the free acid, which involves a considerable reduction in the stabilizing effect of the hydrions; (2) the adsorption of hydrions by the hide gel when first immersed in approximately neutral condition; (3) the operation of the "valency rule" that the predominant ionic effect in discharging is due to the multivalent anions. In this case the divalent SO_4'' ion assist materially in discharging the positive charge on the chrome sol; (4) the final process of neutralization in which still more alkali is added. The operation of the valency rule is the most complex of these factors, for there is also to be considered the stabilizing effect of the kations, especially of the trivalent kation Cr''' from the unhydrolized chromium sulphate. It is quite possible also that in the last stages of chrome tanning there are "zones of non-precipitation" due to the total effect of multivalent ions, and it is quite conceivable that the chrome sol may change its sign—*i. e.*, become a negative sol and thus give also a mutual precipitation with the hide-gel. This is particularly probable where a local excess of alkali occurs in neutralization. However that may be, it is probable that most of the tannage is accomplished by chromium hydrate in acid solution, and it is, therefore, legitimate to conclude that adsorption and gelation have a relatively greater part in chrome tannage. The operation of the valency rule makes it easy to understand why basic chlorides do not tan so well as sulphates; the precipitating anion is only monovalent (Cl'), and chromic chloride contains no substance analogous to the potassium sulphate of chrome alum, and, hence, contains a less concentration of the precipitating anion. Hence, also, the stabilizing influence of common salt added to a basic alum liquor, the effect being to replace partially the divalent SO_4'' by the monovalent Cl'. Wilson has recently (*Collegium*, 1917, p. 108, from *J. A. L. C. A.*, 1917, p. 458) questioned this, on the strange

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contention that "the addition of even small quantities of electrolytes to chromium hydroxide sols results in precipitation." It need hardly be pointed out that such small quantities so operate only on the practically pure or dialyzed sol, while in chrome liquors the sol is in acid solution, the most favorable circumstance for a stable positive sol!

It is possible to make out a rather weak case that the tanning sol is not chromium hydrate at all, but a basic salt of chrome also in colloidal solution, and to contend that this salt, like most substances, forms a negative sol, but in practice not negative enough, hence the desirability of alkali, divalent anions, etc. From this point of view the analogy with vegetable tannage becomes more complete, and the stabilizing effect of the soda salts of organic acids becomes easy to understand.

It is highly probable that the electrical properties of the chrome sol need closer investigation on account of the complexity due to the prominent effect of multivalent ions. It is desirable to bear in mind the remarkable phenomenon observed by Burton (*Phil. Mag.*, 1905, **12**, p. 472), who added various concentrations of aluminium sulphate to a silver sol (negative). He observed (1) a zone of non-precipitation due to protection; (2) a zone of precipitation due to the trivalent kation; (3) a second zone of non-precipitation due to protection after the sol has passed through the iso-electric point and become a positive sol; (4) a second zone of precipitation due to the precipitating effect of the anion on the now positive sol. It seems to the writer that similar phenomena may possibly occur in chrome tanning, for whatever the sol actually is, it is not far from the iso-electric point.

A few observations on the vegetable-chrome combination tannages will not be out of place at this stage. Wilson refers to the well-known practical fact that chrome leather can take up about as much vegetable tan as if it were unchromed pelt, and considers this evidence that the two tannages are of fundamentally different nature. "In mineral-tanned leathers the metal is combined with carboxyl groups, while in vegetable-tanned leather the tannin is combined with the amino groups. This strongly suggests the possibility that the two methods of tanning are to some extent independent of one another, and that a piece of leather tanned by one method may remain as capable of being tanned by the other method as though it were still raw pelt" (*Collegium*

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(London), 1917, pp. 110-111). To the writer, however, it seems that the facts are evidence for the contrary proposition, that the tannages are fundamentally of the same nature. On the adsorption theory, one would expect chrome leather to adsorb as much tan as pelt; the readily adsorbable tan is the same, and the chrome leather is an adsorbent of very much the same order of specific surface as pelt. The adsorption theory would find it difficult to account for chrome leather not adsorbing as much tan as pelt. It is quite conceivable that a chrome leather could adsorb more tan than pelt, owing to the more complete isolation of the fibrils by the chrome tannage and to their being coated over by a more adsorbent gel. Adsorption is often deliberately increased by a preparatory adsorption. Thus sumac-tanned goatskins are wet back from the crust and "re-tanned" in sumac before dyeing to coat the fibers with a fresh and more adsorbent gel, and so insure the even and thorough adsorption of the dyestuff. Mordanting fabrics has a similar object—the adsorption of colloidogenic substances which give rise to an adsorbent gel on the fiber. Unless vegetable-tanned leather is so much loaded with tan that its specific surface is effectively reduced, one would similarly expect that vegetable-tanned leather would adsorb the chrome sol. This, of course, is exactly the case of semi-chrome leather. If, on the chemical combination theory, the vegetable tan combines with the amino groups and the chrome with carboxyl groups, it is natural to inquire which groups the dyestuffs combine with. As either tannage does not interfere with the adsorption of dye, are we to conclude similarly that tanning and dyeing are fundamentally different processes? Perhaps Mr. Wilson will give us an equation for the formation of leather from pelt by the action of dyestuffs,—a practical though hardly an economic process.

In addition to the various essential actions of tanning hitherto discussed, *viz.*, lyotrope influence, adsorption, diffusion, gelation, and precipitation, there are also changes subsequent to these which previous writers have designated as "irreversible changes." The author confessedly fights shy of this term. The modern developments of colloid chemistry indicate that the old ideas of irreversibility must be revised. Of recent years many so-called "irreversible" changes have been reversed with ease, and with

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the development of knowledge as to the nature of the changes we may expect many more such reversions. Hence, the author is disinclined to admit irreversible changes in tanning. Undoubtedly changes occur after the actual process of tanning which render the tannage more permanent and less reversible, but these changes are, in the writer's opinion, continuations of the various actions discussed above, more particularly the further dehydration of the gel and the electric discharge in mutual precipitation. If this view be correct, then not only are both the vegetable and chrome tannages conceivably reversible processes, but also it is possible to lay down the principles or conditions under which we should most expect to obtain reversion. The problem, in fact, becomes merely to attain conditions which favor the solation of the tanning agent, the solation of the tanning gel, and the solation of the precipitated colloid.

Consider, first, the vegetable tannage. Solation of gels is greatly assisted by preliminary imbibition. Now, when a gel imbibes water heat is evolved, but when a gel solates heat is adsorbed; hence, the more favorable procedure for the solation of a dehydrated gel is first to secure imbibition in cold water and then assist solation by heat. This procedure is usual indeed in making a gelatin solution, in the analysis of tanning materials, and in leather analysis during the estimation of "water soluble matter." It is the first and obvious procedure in stripping vegetable-tanned leather. The solation of the precipitated tan is the more difficult matter, for it involves the return of the electric charge characteristic of the sol. Now some precipitations of colloids are readily reversible, while others are apparently not, and between these extremes lie the majority of sols. In many cases reversibility is a matter of time, and the division into reversible and "irreversible" precipitations depends upon an arbitrary interval of time. This corresponds to the ageing of mineral-tanned leather. The tannins being primarily negative sols, the employment of some reagent which assists the adsorption of hydroxyl ions must evidently be chosen. In practice, therefore, alkalies are used for partial stripping. Unfortunately a complication arises, owing to the oxidation of tannins in alkaline solution, and this renders impracticable the complete stripping by such agents as caustic soda and sodium carbonate. The use of such agents is also impracticable on account of the hydrolysis of the collagen.

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In consequence one is obliged to use only slightly alkaline agents and to consider other methods of imparting a negative charge to the colloid. The use of neutral salts with multivalent anions is naturally suggested by the adsorption theory and the valency rule. The author has experimented with many such salts, and has found that sodium sulphite is one of the most efficient. In this salt we have a weak (adsorbable) dibasic acid, combined with a monacid base, yielding solutions that are alkaline to methyl-orange but not to phenolphthalein. This salt possesses the further advantage that its reducing powers check the tendency to oxidation in even faintly alkaline solution. Its power for solating tannins have also been previously demonstrated in the "solubilizing" of quebracho phlobaphenes. Similar considerations point to borax as an alternative, though less satisfactory in the early stages of stripping, on account of its greater hydrolysis and alkalinity. Borax, also, has been used for the solation of phlobaphenes. In the author's opinion the complete reversibility of the vegetable tannage is quite possible, but its economic exploitation is as yet impracticable owing to considerations of time and expense.

The reversibility of the chrome tannage is an easier proposition, partly because the leather is comparatively much less tanned, and partly because the acidity or alkalinity of the stripping agent may be adjusted, as desired, without the oxidation trouble. In approaching this question from the theoretical side one must consider mainly whether to solate the tanning agent to a positive or to a negative sol. Our imperfect knowledge of the electrical forces in operation in the chrome tannage is thus a serious drawback, but the evidence on the whole points to the precipitation being effected by a negative sol near its iso-electric point, but in faintly acid solution. Hence, we should theoretically expect that reversion should take place into a negative sol in nearly neutral or even faintly alkaline solution. Thus, suitable stripping agents for chrome leather would be the alkali salts of organic acids (especially if multivalent). Now, Procter and Wilson have recently accomplished this stripping of chrome leather by the use of such salts. They approached the question from an empirical and practical point of view, and found that Rochelle salt, sodium citrate, and sodium lactate would strip the chrome tannage with ease. This important and very creditable achievement

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will have great practical and commercial importance. Procter and Wilson have deliberately and carefully refrained from offering an exact explanation of this reversible action, but point out that all their stripping agents are salts of *hydroxy-acids*, and strongly insist that these form soluble complexes with the chrome. While not denying this in the least, the present author would point out that, according to the views advanced in this paper, the salts of organic acids which do not contain hydroxyl groups should, when combined with a monacid base, also strip the chrome tannage. This he has found to be the case. Thus the chrome tannage is reversible in solutions of ammonia or potassium oxalate and of ammonium acetate. With these salts the full effect of multivalent anions is not attained, so that somewhat strong solutions are necessary. A 10 per cent. solution of ammonium acetate shows some stripping effect after a few days, but a 40 per cent. solution after a few hours. Saturated ammonium oxalate is only a 4.2 per cent. solution, but shows a stripping effect in 2 to 3 days. Potassium oxalate (33 per cent.) shows distinct stripping in 24 hours. Potassium acetate and sodium acetate show only slight action, because the solution is too alkaline, but strip if acetic acid be added, until litmus is just reddened. It is noteworthy from a theoretical point of view that a 40 per cent. solution of ammonium acetate is distinctly acid, and indeed smells of acetic acid. There can be little doubt that such stripping actions are also connected with the solubility of the stripping agent in the gel, for the liquid must pass through the walls of the gel to dilute the liquid in the interior. This view fits in with the facts that hydroxy acids and ammonium salts are particularly efficient, for the tendency of chrome to form ammonia-complexes as well as hydroxy complexes is well known. From this point of view we should not expect a stripping action from a salt such as disodium phosphate which would form an insoluble substance. Actually sodium phosphate does not strip, and indeed reduces the stripping power of ammonium acetate. Similarly, we might expect some stripping action by ammonia and ammonium chloride, with the formation af chrome ammonia complexes. This actually occurs, a pink solution being obtained. Sodium sulphite does not strip, possibly partly on account of its too great alkalinity, but is interesting theoretically to observe that sodium sulphite as well as Rochelle salt will strip salt stains

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(see Yocum's patent, *Collegium* (London), 1917, p. 6; also Procter and Wilson, *loc. cit.*). This points to the formation of a negative sol, and suggest many other substances for removing salt stains. Another side issue is that any of the chrome tannage stripping agents might be used to wet back a long dried out heavily chromed-hide powder, though whether an analytical method with such a course is desirable is now doubtful. The above stripping tests were on a chrome leather tanned 4 years ago, dried out without oiling and kept in a warm place.

In conclusion, the author would like to admit that the above re-statement of the theory of tanning is more polemical than experimental. It is true that it involves some extension of earlier adsorption theories, that it explains and correlates many experimental results previously published by the writer, and by others, and that it contains some new experimental facts, but in the main it is due to the normal evolution of colloid chemistry at the hand of many workers. It has been the author's chief care that this theory should be in as complete harmony as possible with our present knowledge of the colloid state. In doing so he feels on much safer ground than in theorizing over a more limited field and in generalizing from experiments with only a few substances. Colloid chemistry is advancing at a much more rapid rate than the experimental investigation of the theory of tanning, so that much of the foregoing theory is almost a necessary corollary of the wider facts of colloid behavior. The author claims merely that he has found the above theory the best explanation of the phenomena of tanning, that it supplies sound guiding principles for practical application, ready explanations for apparent anomalies, and a fertile field for investigation and research.

Much remains still to be done, especially in correlating the valency rule, the lyotrope series, and the adsorption law. These three generalizations of colloid chemistry are of vital importance to the tanning theory, and upon our increased knowledge of these phenomena lies the chief hope of advancement in the theory of leather formation.

Little reference has been possible to the views of Dr. Moeller, as only translations of very vague summaries are as yet available. Meanwhile, his apparent view that the real tanning

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agents are what one generally terms "insolubles" and "non tans" is almost as startling as Mr. Wilson's blood-curdling equations.

SOL AND GEL CONDITION OF GELATIN SOLUTIONS. PART II. SWELLING.*

By L. Arisz.

Kolloidchemische Beihefte, 1915, Vol. 7, p. 42.

While the first part of this paper, (*Abst. this Jour.*, 1917, p. 536) discussed the changes produced in a a gelatin solution of uniform concentration by variations of temperature, the present part deals with the effects of varied concentration at uniform temperatures. While the changes in solutions can be followed by observation of viscosity, a different method must be adopted in the case of gelatinized solutions which will not flow.

Sols.—A ½ per cent. solution of washed gelatin dried over sulphuric acid, was made at 70° C. and cooled and preserved for 5 days at 20°, and was then diluted to ¼ per cent. The viscosity was of course much reduced by dilution, and in a portion kept at 20° C. continued to diminish. On the other hand, that of a portion heated to 70° was at once much reduced, and after cooling to 20° gradually increased, so that presumably both solutions would ultimately have reached the same equilibrium viscosity. Another experiment, in which similar solutions were retained at 12° gave analogous results, but the differences in viscosity were much greater, and tended very slowly to equilibrium. This is in complete agreement with the previous work on sols (*loc. cit.*), and shows that a gel, when sufficiently diluted, even when below its melting point, will slowly assume the sol form corresponding to its dilution and temperature.

Jellies.—The method of Hofmeister[1] was adopted, on which blocks of jelly were suspended in a large excess of water, and the degree of swelling from time to time determined by weighing, after wiping with filter paper. For comparative experiments all the blocks were made from the same solution. Thin sheet gela-

* Abstracted in *J. S. L. T. C.*, Nov., 1917, by H. R. Procter, with notes by the abstractor.

[1] F. Hofmeister, *Arch. f. Exp. Path. & Pharm.*, 1890, **27**, p. 395.

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tin swells in water at 30°, separates into flocks, and gradually dissolves. Solution is complete in 24 hours. At 35°, 2½ hours only is required, and at 50° only about 2 minutes. Below about 30° the gelatin swells, but does not dissolve. The swelling, rapid at first, either ceases at some point which it tends to, or goes on with extreme slowness. At 25°, (which is near the melting point) it is apparently without limit, and at 12° some slight increase was observed even after 3 weeks. Arisz does not attempt to decide the point whether the swelling tends to a definite maximum, but inclines to the view that there is a maximum corresponding to the state of dilution and temperature, but that slow changes of condition take place, tending to higher maxima.

Note.—It is very difficult to avoid all risk of bacterial action in long continued experiments with warm gelatin solutions, and even in absence of bacteria it is not unlikely that slow change of the nature of hydrolysis may occur. Theory also indicates that a change such as swelling, which proceeds at a constantly diminishing speed cannot actually reach that maximum infinite time.

Arisz's view is that the swelling and solution are two stages of the same process, and of course infinite swelling must amount to solution, but there is a good deal of evidence that the aggregation below the melting point is different to that above it, even though in both cases a liquid is produced. *Abst.*

Influence of Concentration on Swelling.—The method of experiment adopted was as follows: Thin sheet gelatin (presumably washed) was dried over sulphuric acid and weighed, and then exposed to saturated water vapor, of which it absorbed about one-fourth of its weight. This jelly was liquified at 70°, diluted with water to the required concentration, and after complete mixture was cast in moulds to blocks of 33 × 7 × 4 millimeters. Blocks were made of 80, 50, 20 and 10 per cent. and immersed in water for various periods, and the gain of weight, was noted after blotting off adhering water. Eighty per cent. was the maximum possible concentration, since beyond this the jelly will not liquify at 100°. As by this procedure the water was obviously, at any given time, unequally distributed in the blocks, the gain of weight was simply stated as a percentage of the actual gelatin in the block, which was reckoned as unity.

Note.—It is obvious that the gain of weight thus stated is a very complex function, of which it is not easy to visualize the significance, and it is probable that the anomalous effects observed in several cases were due

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partly to this and partly to the unequal distribution in the blocks, which of course tended to equalize itself as the time of soaking was extended, owing to internal diffusion in the block. This last point is noted by Arisz. The rate of absorption is largely if not mainly dependent on the rate of diffusion, as was pointed out by Hofmeister, and therefore is greatly affected by the size, and especially the thickness of the blocks, and the method of experiment does not seem well adapted to give general and intelligible results. Arisz alludes to the deformation of shape of thick blocks in the early stages of swelling, from the more rapid adsorption at the edges remarked by Hofmeister, but assumes that in the later stages when this has "nearly" disappeared the distribution is really equal, which is extremely improbable. *Abst.*

The blocks swell not merely when placed in water, but also in more dilute sols, and even in a 1 per cent. solution, which gelatinized, no observable slowing of swelling occurred.

The effect of time is what would be expected from the previous work on sols. Blocks cooled rapidly to 10° and 20° and at once placed in water swell more rapidly, and apparently to a greater extent than others which have previously been preserved at these temperatures for from 1 to 7 days.

If preserved at temperatures other than that of the water in which they are allowed to swell, the result is naturally more complex. The "ripening" takes place more rapidly at 20° than at 10°, but as would be expected, the polymerization or other change opposing swelling does not go so far at the higher as at the lower temperature.

If a jelly-block after say 2 days swelling is removed from water, and preserved in saturated aqueous vapor for a time, and then returned to water, its rate of swelling is at first more rapid than that of a block which has remained in water, and which is therefore already more swollen, so that the swelling of the former tends to overtake that of the continuously swollen block, though it does not actually reach it in a limited time, but, no doubt, would ultimately attain the same maximum.

Note.—The cause of this is not fully explained by Arisz, but obviously depends on the unequal distribution of the water in the layers of jelly, that from the more fully swollen surface gradually diffusing inwards during the stay out of water, and leaving the surface dryer, and therefore able to absorb more rapidly. The process must also be complicated by the time required for the gelatin to reach the state of aggregation corresponding to its new dilution. *Abst.*

If, during its stay out of water, the jelly is exposed to a higher temperature, say 20°, while the swelling takes place at 10°, in-

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ternal changes take place, probably in breaking down of larger to smaller complexes, which increase its capacity for swelling, so that when it is returned to water at 10° the swelling is at first much more rapid, but gradually reverts to the rate proper to 10°. If these alternations are repeated, very complicated curves of swelling are produced, but the final result approximates to that of swelling continuously at the higher temperature. The effect even of so short an exposure to the higher temperature as 15 minutes is obvious, but increases with longer exposures.

It would be expected, therefore, that the effect of transference from water of a lower to that of a higher temperature would be at once to increase the rapidity of swelling, but curiously the change from water of 10° to water of 20° has at first the effect of causing an actual contraction and expulsion of water, while conversely change from 20° to 10° begins by increasing the rate of swelling, which, however, soon reverts to that proper to the temperature at which it is taking place. Still more striking is the observation that if jelly which has been swelling at 10° is removed into a moist atmosphere at 20°, actual drops of water are expelled and appear upon the surface. These effects are not very obvious in the early stages of swelling, but become more marked as the swelling approaches its maximum. The appearance of drops on the surface of a cold jelly brought into a warm, moist atmosphere might be attributed to condensation which could not be rapidly enough absorbed, but this would furnish no explanation of the observed loss of weight in water. Arisz recalls the observation of Bjerkèn,[2] that jellies stretched about 10 per cent. are contracted by heat, and points out that swollen jellies are in a state of tension, and Tyndall in his lectures on "Heat as a mode of motion" refers to a similar effect with stretched rubber, which conversely becomes heated by stretching.

Arisz discusses various theories of jelly structure and of swelling, and points out that the earlier theories of cell-structure only increase the difficulties of explanation by relegating to the cell walls the very properties which it is sought to explain in the mass. It is not easy to form a clear picture of his own views of structure, although he discusses it at considerable length, but

[2] *Wied. Ann.*, 1891, **43**, p. 817.

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from all the complex phenomena described, the following facts seem to emerge.

1.—A change occurs on dilution, requiring time for its completion.

2.—A change dependent on temperature, but also requiring time for its completion. Both dilution and rise of temperature appear to favor a more disperse state, or smaller aggregates of the gelatin.

3.—The jelly structure in which the liquid is held is contracted by heat, either by diminished attraction for the liquid, or increased attraction of the gelatin for itself.

The "previous history" of the jelly, or in other words the extent to which the above changes have already taken place in one or the other direction greatly influences its behavior under any given circumstances.

Paul V. Schröeder[3] stated that jelly which had been fully swollen in water lost moisture when exposed to an atmosphere of saturated water vapor, a circumstance very difficult of explanation if the jelly is really in equilibrium with the water, since it is a law that when two phases are in equilibrium, they are in equilibrium in every respect, and consequently not merely in absorption of liquid water, but also in vapor pressures. V. Shröeder's experiments were apparently conducted with great care and under considerably varied conditions but Arisz was unable to reproduce his results, and inclines to the view that they were due to errors of experiment. V. Schröeder is no longer living, and is unable to defend his experiments, but they certainly demand repetition under precisely the conditions he describes, which were not completely fulfilled by Arisz. V. Schröeder himself suggests that the results were due to the equilibrium not being really a complete one, but still subject to slow time-changes which prevented the process being completely reversible, and Arisz's own work renders this extremely probable. It may however be mentioned that the present writer showed[4] from V. Schröeder's own figures that the forces involved in change of volume near the point of maximum swelling were extremely

[3] *Zeits. f. Physik. Chem.*, 1903, **45**, 109; *c. p.*, also *ibid.*, p. 75, and *Coll.*, 1903, **2**, 201.

[4] *B. A. Reports*, 1908, p, 201.

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small, and of the same order of quantity as the compressive forces of surface-tension arising from the removal of the gelatin from water, and it is by no means certain that this may not be the true explanation.

Arisz's own summary of his results is as follows:—

1.—The theory that a jelly is a system of cells or cavities separated by walls offers no advantage as an explanation of the jelly state.

2.—It may be supposed that the entrance of water in swelling causes a change of size of the gelatin-particles, and probably a diminution of their cohesion; and, conversely, these changes influence the quantity of water which the jelly can absorb.

3.—A jelly which has absorbed its maximum of water undergoes change when it is preserved out of water, either because the gelatin particles are larger, or because the cohesion between the particles is stronger than would be the case if the inner equilibrium were established with a like water-content.

4.—The intensity of the contraction which a swollen jelly suffers on warming is proportional to the resistance which such a jelly offers to further swelling.

5.—The influence of temperature on the velocity of change of gelatin plays an important part in the explanation of observations on swelling and swollen jellies.

Note.—Par. 3 of the above summary is somewhat difficult of comprehension, but the abstractor has confined himself to giving the most accurate translation he could without further comment, the only liberty he has allowed himself being to use the word jelly throughout in place of the more general and less specific gel, since all gelatin-gels are jellies, and the experiments relate only to gelatin-gels, and certainly are not applicable to many of the colloid precipitates which are commonly included under the name of gels.

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NOTE ON THE ALTERATION IN BASICITY DURING THE TANNAGE OF HIDES IN ONE-BATH CHROME LIQUORS.*

By C. F. Barber and P. R. Barker.

The first series of chrome liquors taken consisted of three, made up with chrome alum and sodium carbonate. Tannage was commenced in each case with a liquor of 5° B. in the drum, which was sampled for basicity every half hour, and at the same time strengthened 5° until a gravity of 35° B. was reached.

No. 1	No. 2
75 grms. chrome alum	100 grms. chrome alum
5.3 " soda	5.3 " soda
1 liter water	1 liter water
Basicity as made up = 90.5	Basicity as made up = 104.5

No. 3
125 grms. chrome alum
5.3 " soda
1 liter water
Basicity as made up = 117.1

The basicity at successive half hour intervals during drumming was:

No. 1	No. 2	No. 3
98.5	109.8	117.2
109.4	114.3	117.8
108.6	113.6	116.8
112.0	114.0	115.1
112.2	118.8	115.0
114.1	125.3	111.4
115.1		122.4

In every analysis the acid in the liquor was estimated by titrating with standard sodium hydroxide, using phenolphthalein as indicator. The chromium was determined by oxidizing with sodium peroxide, boiling to decompose excess, adding hydrochloric acid and potassium iodide and titrating the liberated iodine with standard sodium thiosulphate, using starch indicator.

The second series of liquors was made up from potassium bichromate, sulphuric acid and glucose, in the following proportions:

* *J. S. L. T. C.*, Nov., 1917.

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	No. 1	No. 2	No. 3
Water	480 cc.	480 cc.	480 cc.
Potassium bichromate	240 grms.	240 grms.	240 grms.
Sulphuric acid	200 "	200 "	200 "
Glucose	280 "	240 "	200 "
Basicity as made up	80.9 "	87.5 "	110.2 "

The basicity, at successive intervals of three-quarters of an hour, was as follows :

No. 1	No. 2	No. 3
96.7	86.8	68.5
87.2	76.5	76.5
89.0	75.6	77.3
81.4	77.1	76.5
86.3	75.3	89.9
88.6	76.0	77.3
83.9	79.4	104.2
88.0	77.3	81.7

These liquors were made up by boiling the potassium bichromate in water until dissolved, cooling down to 50° C. when the sulphuric acid was added. The boiling solution of glucose was then added to this liquor. The whole mixture boiled during the operation owing to the vigorous reaction.

In order to investigate the influence of temperature during the reaction, three liquors were made up, using exactly the same quantities of materials in each case but varying the temperature.

	Basicity
1. Made up as above and allowed to boil during operation	75.5
2. Never allowed to rise above 90° C.	88.8
3. " " " " 70° C.	92.0

The third series was made up from commercial one-bath liquor. The first number in the series was the original liquor, while the others were made from it with the addition of definite amounts of strong sulphuric acid.

Original basicity was 76.

Commencing basicity of each number :

No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
76.0	89.1	99.8	113.4	127.3	139.5

Basicity at successive intervals of three-quarters of an hour :

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80.8	99.1	100.4	113.0	119.8	136.0
81.2	102.7	100.3	118.3	127.1	133.3
80.1	90.7	105.3	116.7	127.2	136.0
79.6	91.1	93.5	113.1	122.0	136.0
81.2	86.6	97.7	118.9	119.0	131.3
87.6	90.3	101.3	118.3	124.0	139.1
—	97.8	99.7	113.9	123.0	—
—	—	—	111.1	129.4	—

A fourth series of liquors was made up from potassium bichromate, sulphuric acid and sodium thiosulphate, as follows:

No. 1	No. 2	No. 3	
250	250	250	grams potassium bichromate
450	450	450	cc. water
150	175	200	cc. sulphuric acid
275	275	275	grams sodium thiosulphate
120.4	135.6	153.2	basicity as made up

The basicity at successive intervals of three-quarters of an hour was:

110.4	132.4	140.4
116.7	—	146.3
116.3	128.8	141.7
114.2	127.3	143.9
110.4	127.8	145.0
113.8	124.2	149.2
109.9	130.4	148.2
112.9	128.6	147.7

English hides were used in the tannage, of about 60 pounds' weight, and were delimed by means of a mixture of formic and lactic acids, and subsequently bated with an artificial bating material containing a great amount of ammonium chloride.

ABSTRACTS.

Outline of Colloid Chemistry, I. W. D. BANCROFT. *J. Franklin Institute*, **185**, 1918, pp. 29-57. The author reviews and discusses the effects, rather than the causes, of adsorption, giving 146 references and numerous illustrative examples. The subject matter is divided into eight parts.

Introduction.—Graham's distinction between crystalloids and colloids has been dropped and one now speaks of a colloidal state instead of a colloidal substance, calling any substance colloidal which is sufficiently subdivided. Colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films and a knowledge of it is essential to anybody who wishes to understand about: cement, bricks, pottery, porcelain, glass,

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enamels; oils, greases, soaps, candles; glue, starch, and adhesives; paints, varnishes, lacquers; rubber, celluloid, and other plastics; leather, paper, textiles; filaments, casts, pencils and crayons; inks; roads, foundry cores, coke, asphalt; graphites, patines, zinc, phosphorous, sodium, and aluminum; contact sulphuric acid, hardened oils, etc.; beer, ale, and wine; cream, butter, cheese, and caseine products; cooking, washing, dyeing, printing; ore flotation, water purification, sewage disposal; smoke prevention; photography; wireless telegraphy; pharmacy; physiology. In other words, colloid chemistry is the chemistry of daily life.

Adsorption of Gases and Vapors by Solids.—In an extremely subdivided phase the surface is very large compared to the mass, and therefore, the first step in the study of colloid chemistry is to discuss the properties of surfaces, beginning with the behavior of solids in contact with gases or vapors. All solids tend to adsorb, or condense, upon their surfaces any gases or vapors with which they are in contact. The amount of adsorption varies with the nature and physical state of the solid and with the nature of the gas, *i. e.,* adsorption is specific or selective. The amount of gas adsorbed is greater the higher the pressure and lower the temperature. Experiments have been made with many substances such as charcoal, silica, alumina, glass, wool, rubber, celluloid, meerschaum, metals, soils, etc.

An extensive study has been made of the adsorption of gases by charcoal because this substance adsorbs many gases very strongly. Tait and Dewar used this property as a means of producing a high vacuum, while it has been put to use in a more popular fashion in certain digestive tablets containing charcoal, whose function is to adsorb gases in the stomach which would otherwise give rise to discomfort. Since different gases are adsorbed in different amounts, the ratio of their concentrations in the surface phase will be different from that in the gas phase, making a fractional separation possible to some extent. Dewar passed air at —185° over charcoal and obtained 98 per cent. nitrogen, while the adsorbed gas contained 55 per cent. oxygen.

Adsorption by glass is important because of its use in the laboratory. Mulfarth found that adsorption decreased in the order NH_3, SO_2, CO_2, N_2O, C_2H_2. Kundt and Warburg found that a small amount of water is retained obstinately by glass, even when the pressure is reduced practically to zero; in order to remove this water, the glass must be heated. The film of water which usually covers glass surfaces is due chiefly to alkali dissolved from the glass. The presence of a water film of varying thickness on a glass or other vessel makes it necessary to keep the moisture constant, if accurate weighings are to be made.

If the thickness of the adsorbed air film remains constant while the diameter of a particle grows smaller, the ratio of quantity of adsorbed air to the mass of the particle will steadily increase. Rock powder that will pass through a 200-mesh sieve surges like a liquid, due to the air cushions around each particle. With carbon black, as little as 5 per cent. of the apparent volume may be due to carbon. In adsorption the surface

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phenomena are the important ones, although other factors, such as the existence of a solid solution, may influence actual results. The bulk of the 100 volumes of hydrogen taken up by platinum black and the 3,000 volumes by colloidal platinum must be adsorbed.

An approximately quantitative representation of adsorption of gases by solids is given by the equation

$$(x/m)^n = kp,$$

where x is the amount of gas adsorbed, m the amount of the adsorbing solid, p the pressure of the gas, and k and n are constants to be determined experimentally for each temperature.

Catalytic Action of Solids on Gases.—When two or more gases which combine or react with each other are adsorbed at the surface of a solid, since their concentrations are increased, they must react with greater velocity. It is possible that the ignition of hydrogen and oxygen by spongy platinum may be due solely to this increased concentration. On the other hand, the fact that charcoal has but little effect in causing these gases to combine indicates that some other factor is important in addition to surface concentration. A solvent may accelerate a reaction and is therefore a catalytic agent. If a reaction takes place extremely slowly in the vapor phase and relatively rapidly in the surface phase, the adsorbing surface may be considered as equivalent to a solvent. If a strongly adsorbed gas is added to a reacting mixture, it may cut down the adsorption of the reacting substances to such an extent as to bring the reaction practically to a standstill, which may be the explanation of the poisoning of a catalyst. If certain reaction products are not removed sufficiently rapidly, they will decrease the adsorption of the reacting substances, thus retarding the reaction. SO_3 may have this effect in the contact process.

Adsorption of Gases or Vapors by Liquids.—Gases are adsorbed by liquids just as they are by solids. Impinging drops of water often will not coalesce because films of adsorbed air keep them from coming into actual contact. If they are slightly electrified, however, they readily coalesce, but stronger electrification keeps them apart. It is possible to knock two soap bubbles together with considerable force without causing them to coalesce, because of the presence of adsorbed air films on the surfaces. If the bubbles are electrified slightly, they coalesce readily without bursting.

Adsorption of Liquids by Solids.—A liquid which is adsorbed at the surface of a solid forms a film there, and we say that the liquid wets the solid. A liquid is not adsorbed by a solid which it does not wet. For a liquid to wet a solid in the presence of air, the liquid must be more strongly adsorbed than the air and must displace it. The adsorption of a liquid film may introduce an error in the determination of specific gravity of solids in a finely divided state. Rose obtained a specific gravity between 21 and 22 for platinum foil, but a value of over 26 for finely divided platinum and explained in the latter case that the solid is not weighed alone, but in conjunction with a film of condensed water and

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the apparent specific gravity is increased. As examples of selective adsorption we find that kerosene will displace water in contact with copper, but water will displace kerosene in contact with quartz. Gelatin is so strongly adsorbed by glass that the gelatin film in drying will often tear loose fragments of glass, while on the other hand, gelatin does not adhere to plates of mica or calcite.

Adsorption of Solids by Solids.—An apparent case of adsorption of a solid by a solid is obtained by shaking a moderately coarse powder with a much finer powder. Instead of the finer powder filling the voids in the space occupied by the coarse powder, the former tends to coat the latter. By shaking mixtures of powdered thoria and tungsten, Fink obtained a black powder which conducted electricity when the tungsten was finer than the thoria and a white, non-conducting powder when the reverse was the case. If one strews lycopodium powder over the surface of water and then puts his finger into the water, the powder sticks to the finger and keeps it from being wetted.

Adsorption of Liquids by Liquids.—If an oil is adsorbed by water, it will spread over the surface of the water, but if it is not adsorbed, there will be no spreading.

Adsorption of Solids by Liquids.—A solid which is wetted by a liquid adheres to that liquid and with two liquids and one solid we get selective adsorpton of the solid. It was noted above that kerosene will displace water in contact with copper. Similarly, if very fine copper powder is shaken up with kerosene and water, the copper goes into the kerosene and into the interface, but not into the water, producing the appearance of molten copper floating on the water. J. A. W.

The Fallacy of Determining Electrical Charges of Colloids by Capillarity. A. W. THOMAS AND J. D. GARARD. *J. Am. Chem. Soc.*, **40**, 1918, pp. 101-106. Under the title "Capillary Analysis," Wo. Ostwald has recommended a method proposed by Sahlbohm and Fichter for distinguishing between positively charged and negatively charged colloids, in which it is supposed that negatively charged colloids ascend strips of filter paper which are dipped into their dispersions, while positively charged colloids do not ascend, but coagulate on the paper a slight distance above the level of the dispersion into which the paper is dipping. The method has been widely used because of its simplicity, but it is now shown to be fallacious, the observations of earlier investigators being due to the fact that their positively charged colloids were concentrated while their negative colloids were dilute. Thomas and Garard find that the height to which a colloid will ascend a strip of filter paper immersed in its dispersion is dependent upon the dilution of the sol, the presence of electrolytes, the atmospheric conditions, and the nature of the filter paper used, but bears no relation to the sign of the electrical charge of the colloid. J. A. W.

On the Swelling of Gelatin in Polybasic Acids and Their Salts. M. H. FISCHER AND M. O. HOOKER. *J. Am. Chem. Soc.*, **40**, 1918, pp. 272-92. Thirteen series of experiments were made to determine the amounts of

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water absorbed by gelatin discs immersed in different concentrations of the mono-, di-, and trisodium salts of phosphoric and citric acids as well as in mixtures varying in composition from the pure acids, through the mono-, di-, and trisodium salts to pure sodium hydroxide. A further series was made with mixtures of carbonates varying from sodium bicarbonate, through sodium carbonate, to pure sodium hydroxide. The results of a typical series are tabulated in the accompanying table. Into each of the thirty-one solutions described in the table was placed a dry gelatin disc of the weight noted. At the end of the stated periods of time, the swollen discs were weighed in order to determine the amount of absorbed water.

Solution No.	Original solution consists of mixture of: cc. N/1 H_3PO_4	cc. N/1 NaOH	cc. H_2O	Weight of dry gelatin disc in gram	Increase in weight per gram of gelatin after: 20 hours	44 hours
1	3	none	97.0	0.343	69.32	84.68
2	3	0.1	96.9	0.343	62.85	75.11
3	3	0.2	96.8	0.345	58.65	70.60
4	3	0.3	96.7	0.347	58.45	69.90
5	3	0.4	96.6	0.360	46.60	58.17
6	3	0.5	96.5	0.363	43.00	54.16
7	3	0.6	96.4	0.365	31.00	42.20
8	3	0.7	96.3	0.367	22.31	33.87
9	3	0.8	96.2	0.367	15.30	24.32
10	3	0.9	96.1	0.367	8.31	11.28
11	3	1.0	96.0	0.367	7.10	8.27
12	3	1.1	95.9	0.370	8.03	9.41
13	3	1.2	95.8	0.370	8.68	10.27
14	3	1.3	95.7	0.370	8.74	10.44
15	3	1.4	95.6	0.371	9.35	11.16
16	3	1.5	95.5	0.374	9.60	11.56
17	3	1.6	95.4	0.380	9.49	11.31
18	3	1.7	95.3	0.382	9.81	11.60
19	3	1.8	95.2	0.383	9.81	11.57
20	3	1.9	95.1	0.384	10.00	11.90
21	3	2.0	95.0	0.386	10.23	12.14
22	3	2.1	94.9	0.385	10.26	12.40
23	3	2.2	94.8	0.388	10.80	12.61
24	3	2.3	94.7	0.388	11.28	13.12
25	3	2.4	94.6	0.388	11.52	13.00
26	3	2.5	94.5	0.388	13.14	14.24
27	3	2.6	94.4	0.389	15.81	16.25
28	3	2.7	94.3	0.391	15.57	16.17
29	3	2.8	94.2	0.391	17.71	18.03
30	3	2.9	94.1	0.392	19.40	19.37
31	3	3.0	94.0	0.394	19.91	20.50
—	none	none	100.0	0.394	7.45	8.80

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It is to be especially noted that the point of minimum swelling occurs in the solution which is practically pure monosodium phosphate and that the addition of either acid or alkali to this solution will cause increased swelling. In the other series dealing with changes in acidity of phosphate mixtures the point of minimum swelling invariably occurs in the solutions of pure monosodium phosphate. [Unfortunately the authors appear not to have determined the compositions of the solutions after equilibrium has been established, so that it is impossible to calculate from their work the relation between the point of minimum swelling and the hydrogen-ion concentration.—ABSTRACTOR.] In the citrate mixtures, the point of minimum swelling occurs in the solution made by diluting 4 cc. of M/1 monosodium citrate and 6 cc. of M/1 disodium citrate to 100 cc. As for the carbonate mixtures, gelatin swells more in pure sodium bicarbonate solution than in water and this swelling increases steadily as the solution is made more strongly alkaline.

The authors claim that their experimental results apply to the problem of water absorption by protoplasm and sustain the old contention that, even in the presence of buffer salts, there is an increase in water absorption (increased turgor or edema) for every increase in the acid (or alkali) content of the protein colloids found in the involved cell, organ or organism. J. A. W.

On the Swelling of Fibrin in Polybasic Acids and Their Salts. M. H. FISCHER AND M. BENZINGER. *J. Am. Chem. Soc.*, **40**, 1918, pp. 292-303. This work is a continuation of that described in the preceding abstract and was undertaken to show that the behavior of gelatin is not exceptional and that the same general law holds for the absorption of water by fibrin. The fibrin was prepared from blood, washed, dried, and pulverized in a mortar. Weighed amounts of the powder (0.5 gram) were introduced into definite volumes (20 cc.) of the various solutions employed, contained in calibrated test-tubes of uniform diameter (1.5 centimeter). The same standard solutions of acids, alkali, and salts as were used in the work noted in the preceding abstract were used in this work. The height of the swollen fibrin columns, at the end of 24 hours, was taken as the index of water absorption. The curves for fibrin are of the same general character as those obtained for gelatin, but in both the phosphate and the citrate mixtures, the point of minimum swelling of the fibrin occurs in the solutions containing molar equivalents of the monosodium and disodium salts. The authors emphasize that such differences in the point of minimum swelling of various proteins must be kept in mind when these experiments on simple protein colloids are applied to biological materials, since protoplasm represents a mixture of at least two different proteins. [The abstractor is of the opinion that the authors are not justified in concluding from their results that gelatin and fibrin have different points of minimum swelling, since the compositions of the solutions are altered by the proteins during the attainment of equilibrium and apparently no analyses have been made of the solutions after equilibrium has been established.] J. A. W.

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On the Liquefaction or "Solution" of Gelatin in Polybasic Acids and Their Salts. M. H. FISCHER AND W. D. COFFMAN. *J. Am. Chem. Soc.*, **40**, 1918, pp. 303-312. The quality of the gelatin used was of such high grade that an 0.8 per cent. solution would set to a solid mass when left for a few hours at 25°. In each experiment 5 cc. of a 2 per cent. gelatin solution and 5 cc. of the electrolyte solution were mixed in test tubes and allowed to stand in a thermostat at 20°. The electrolyte solutions employed were phosphate, citrate, and carbonate mixtures of the type noted in the abstract of the paper by Fischer and Hooker. At the end of a suitable period of time the gelatin mixtures were examined as to their consistency. The mixture containing pure citric acid would not set, but remained liquid. As the acidity was reduced, the consistency increased. The mixture containing 0.6 cc. N/1 citric acid and 1.6 cc. M/4 monosodium citrate per 10 cc. set to a solid and all mixtures whose acidities lay between this and that of pure trisodium citrate set to a solid. All mixtures with alkalinities greater than that of trisodium citrate remained liquid. Similar results were obtained with phosphate and carbonate mixtures.

The authors are of the opinion that the size of the gelatin particles decreases with increasing concentration of acid or alkali beyond certain limits, while as the acid or alkali concentration decreases, approaching these limits, the size of the particles increases. The capability for absorbing water is held to be a function of the size of the particles, a medium-sized particle being capable of absorbing most water. It is contended further that in neutral gelatin the particles are large and so only a small amount of water is absorbed; when acid is added, the particles become smaller, and therefore, absorb more water; but upon a further addition of acid the particles become smaller than that required for maximum swelling and the mixture begins to liquefy. J. A. W.

The Molecular Mechanism of Colloidal Behavior, I. The Swelling of Fabrin in Acids. R. C. TOLMAN AND A. E. STEARN. *J. Am. Chem. Soc.*, **40**, 1918, pp. 264-272. In the experiments, special test tubes of uniform cross-section and with flat bottoms were used. Into each was placed 0.3 gram of powdered blood fibrin which was covered with 15 cc. of the desired solution. The samples were allowed to stand for 24 hours with occasional shaking. The heights to which the fibrin rose (compared with a water control) were taken as a measure of the degree of swelling. The amount of electrolyte adsorbed by the fibrin was calculated as the product of the volume of the original solution and the loss in concentration after equilibrium has been established. [This method of calculation is in error since it assumes that the concentration of free electrolyte in the absorbed solution is the same as in the residual solution, which is contrary to fact. The adsorption curves given are, therefore, rendered of doubtful value.—ABSTRACTOR.] Experiments were made with strong and weak acids and with salt. The swelling curves obtained are of the familiar type, such as are obtained with gelatin. [See Procter, this JOUR., 6, 1911, p. 270.]

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Tolman and Stearn explain the molecular mechanism of the swelling of proteins by acids as follows: "In an acid solution, the adsorbed hydrogen ions, together with a corresponding number of anions, form a 'double layer' on the walls of the pockets or pores in the interior of the gel and this leads to swelling and imbibition of water by electrostatic repulsion. The addition of a strong electrolyte to such a swollen colloid, either a neutral salt or excess of the strong acid which caused the original swelling, will furnish ions in the interior of the pockets which will tend to arrange themselves so as to neutralize the electrical fields of the adsorbed layer and thus bring about a reduction of swelling."

[It is interesting to contrast this theory with that given by Procter and Wilson (see this JOUR., 11, 1916, p. 399). Tolman and Stern believe that the force causing swelling is one of *electrostatic repulsion,* while Procter and Wilson hold that it is due to the *diffusion pressure* of the necessary excess of diffusible ions of the jelly phase over that of the external solution.—ABSTRACTOR.] J. A. W.

Philippine Tan Barks. *J. S. C. I.*, 1917, p. 1106. Through the *Leather World.* Only mangrove and camanchili barks are used at present in the Philippine Islands for tanning purposes, and as the use of either bark is attended with disadvantages, other barks have been investigated with a view to their utilization. Of those tested only two, the Philippine pine (*Pinus insularis*) and palo maria (*Calophyllum inophyllum*) are both satisfactory in quality and sufficiently plentiful. Neither is rich in tannin, the former containing 3.8 per cent. and the latter 11.9 per cent. tannin, calculated on the dry material. Other barks are richer in tannin and yield leather of good quality, but cannot be collected economically.

Tanning in Australia. *J. S. C. I.*, 1917, p. 1076. Through the *Leather World.* The two wattle barks "golden wattle" (*Acacia pycnantha*) and "black" or "green" wattle (*Acacia decurrens*) form the chief sources of tanning bark. This is now being supplemented by imports of Natal wattle bark from South Africa. Mallet bark (*Eucalyptus occidentalis*) has been used, but only small quantities remain. It is stated that the presence of red coloring matter in mangrove prevents this bark being used to any extent. The redgum (*E. calophylla*) is fairly rich in tannin, but also contains a red coloring matter. For this reason extracts manufactured from these materials have to be decolorized. The report also says "that before the war large quantities of Australian barks, including those of wattle, mallet, and mangrove, were utilized in Germany for the production of extracts and these German extracts were imported into Australia. Chemical research in Germany had solved the problem of decolorization and of the removal of the undesirable gummy matter, and these problems should be investigated in Australia.

The Determination of Ammonia in Used Lime Liquors. F. C. THOMPSON and KYOHEI SUZUKI. *J. S. L. T. C.*, Nov., 1917. The authors used two

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methods in determining the ammonia. The first or usual method was distilling at 100°C. with excess of magnesia after neutralizing the liquor.

The second method was the same as the first, except that distillation was carried out *in vacuo* at a temperature of 40° C. Slightly lower results were obtained in all samples by the second method. The authors suggest that the difference in ammonia content may be due to the presence in the used lime liquors of amino-acid cystine which is derived from the proteins of the hair and epidermis.

Cystine is easily decomposed by magnesia at 100° C., yielding ammonia, but at 40° C. cystine is unaffected by magnesia.

Ammonia is completely liberated from ammonium salts by magnesia at both 100° and 40° C.

A cut and description of the apparatus used for distilling *in vacuo* accompanies the original article.

The Estimation of Fat in Commercial Egg Yolks. M. C. LAMB AND A. HARVEY. *J. S. L. T. C.*, Dec., 1917. The usual method is to evaporate to dryness with sand and extract with petroleum ether, but is open to some errors, due to oxidation and mechanical loss.

The writers have adapted the Adam's method of fat estimation in milk to the estimation of fats and oils in commercial egg yolk.

The method is carried out as follows:

The egg yolk is spotted on to an Adam's paper, or in the absence of this a strip of fat free filter paper (the coarser varieties being preferable for the purpose). The paper is next dried at room temperature over night and then extracted as usual in a Soxhlet apparatus.

The process has been found to be extremely convenient when dealing with a number of samples; the tedious grinding up of the sand and yolk mixture being avoided, while accuracy, together with speed, is obtained.

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Joseph R. Lorenz, % Wm. F. Mosser Co., Richwood, W. Va.

ASSOCIATE.

Frederick W. Dixon, 409 Pine St., Jamestown, N. Y.
Fayette A. Shaw, % Michigan Tanning & Extract Co., Escanaba, Mich.
Dennis E. Bergem, 135 Front St., New York, N. Y.

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CHANGES OF ADDRESS.

Fini Enna, Low Mill Tannery, Ulverston, Lancashire, England.
R. P. Cushing, % Kistler Leather Co., Lock Haven, Pa.
F. O. Sprague, % Beardman & Co., Acton, Ontario, Canada.
W. K. Lewis, 85 Lombard St., Newton, Mass.
Jerome S. Rogers, Box 792, Lock Haven, Pa.
Paul Hayes, 2314 18th St., N. W., Washington, D. C.
V. G. Lumbard, % Ohio Leather Co., Girard, Ohio.
Henry Windt, % Kullman, Salz & Co., San Francisco, Cal.

FIFTEENTH ANNUAL MEETING.

The fifteenth annual meeting of the American Leather Chemists Association will be held at the Hotel Traymore, Atlantic City, May 16th, 17th and 18th, in connection with the meeting of the National Association of Tanners.

The program committee has not completed its arrangements, but the following outline for the joint meeting has been planned:

On Thursday the 16th, each association will hold separately their first session. At the middle of the day the National Association of Tanners will have a luncheon to which all in attendance at the convention will be invited. Following the luncheon there will be a number of addresses given by speakers secured by Mr. Wallin. Friday the 17th, a joint session will be held, for which a program of mutual interest is being arranged.

Saturday separate meetings will be held, concluding the program.

RATES PER DAY—HOTEL TRAYMORE, ATLANTIC CITY.

One person, American plan.....	$7, $8, $10, $11, $12, $14
One person, European plan.....	$4, $5, $7, $8, $9, $10
Two persons, American plan.....	$11, $12, $14, $15, $16, $18
Two persons, European plan.....	$5, $6, $8, $9, $10, $12

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COUNCIL MEETING.

A Council meeting was held at the Chemists' Club, New York City, February 16, 1918. Those present were Messrs. Oberfell, Small, Alsop, Veitch, Yocum and Reed. Mr. J. B. Churchill of the American Leather Research Laboratory was present by invitation.

A letter was received by the Secretary from a member of the Association handing in his temporary resignation to be in effect for the duration of the war as he was now in the service, and did not feel at liberty to continue his subscription.

After discussion it was decided that any member of the A. L. C. A. who has joined the service, on application to the Secretary, may have his dues remitted for the duration of the war and yet retain all the privileges of the Association.

The Committees appointed at the last meeting were reviewed as follows:

The Committee on the question of Disinfection of Hides to co-operate with the National Association of Tanners consisting of Mr. Alsop and Mr. Levi was increased by the addition of Mr. Churchill, who was working along the same lines.

Mr. Guy T. Creese asked to be relieved of the chairmanship of the Committee on Natural Dyes and Mr. C. R. Delaney was appointed in his place.

Mr. Frey, chairman of the Committee on Specifications for Kaolin, Mr. Griffith, chairman of the Committee on Comparative Analysis, and Mr. J. S. Rogers, chairman of the Committee on Free Sulphuric Acid in Leather, reported work under way.

Word was received from Dr. Balderston that he was making good progress on the ten-year index for the JOURNAL.

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THE DETERMINATION OF FAT IN LEATHER.

By John Arthur Wilson and Erwin J. Kern.

A curious incompatibility is manifest in the methods of the Association, for in the provisional method for analysis of moellons use is made of the insolubility of oxidized fatty acids in petroleum ether, while this solvent is required for the determination of fat by the official method for analysis of vegetable-tanned leather. It is not uncommon to find that the oxidized fatty acids constitute more than 15 per cent. of the total fatty matter of a moellon, so that where this material has been used in fat-liquoring, appreciable errors may be expected in the determination of fat in the leather. Even where a sulphonated oil has been used as the emulsifying agent, low results will be obtained because of the insolubility of most hydroxylated fatty acids in petroleum ether.

A possible solvent for oxidized and hydroxylated fats is ethyl ether, which has the advantage of a low boiling point, but the disadvantage of being very inflammable. Carbon tetrachloride, on the other hand, is not inflammable, but has a rather high boiling point. These solvents, as well as a mixture of equal volumes of the two, were tested by comparison with petroleum ether to determine their solvent powers upon the fat of a piece of vegetable-tanned leather known to contain some oxidized fats. The leather was cut into small pieces and well mixed so that all samples taken should be practically identical in composition. For each test 7 grams of the sample were extracted in a Soxhlet apparatus for 5 hours and then for 3 hours longer. The heating devices were regulated so that the various solvents siphoned over about six times per hour. Lest any differences in the fat determinations should be attributed to solution of the water-soluble matter, all four samples were further extracted with water according to the official method. The results are given in Table I.

TABLE I.—SHOWING PARTS OF EXTRACTED MATTER PER 100 PARTS OF LEATHER.

Solvent used for fat determination	Petroleum ether	Carbon tetrachloride	Ethyl ether	Equal volumes of ethyl ether and carbon tetrachloride
Fat extracted in 5 hours	7.79	9.67	10.04	10.39
Total fat extracted in 8 hours	7.92	9.88	10.24	10.59
Water soluble matter	4.90	4.69	4.51	4.43
Total extracted matter	12.82	14.57	14.75	15.02

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The inferiority of petroleum ether as a solvent for fat in this leather seems unquestionable. The greatest difference in fat determination is 2.67, while that for water solubles is only 0.47, so the bulk of this extra 2.67 cannot be said to be matter soluble in water. Upon examination the petrol extract was found to contain no oxidized fatty acids. But, on the other hand, the oxidized fatty acids constituted only 5 per cent. of the extract by the mixed solvents, which suggests that the leather contained fatty matter which was not extracted by petroleum ether and yet which would not appear as oxidized fatty acids in the provisional method for analysis of moellons.

It was noted that the mixed solvents distilled at a somewhat greater rate than the pure ethyl ether, which may account for the slightly higher results of the former. To test this and to show that the inferiority of petrol is not due to a time factor, we extracted two further portions of the sample for 8 days, one with petrol and the other with ethyl ether. The amount extracted by petrol was 8.38 per cent. and that by ethyl ether 10.66 per cent.

When using the mixed solvents, the portion of tetrachloride distilling over with the ether will depend upon the ratio of the capacity of the Soxhlet tube to the volume of solvent employed. In a test case 50 cc. each of ethyl ether and carbon tetrachloride were mixed in a Soxhlet flash and 50 cc. of the distillate, when collected, were found to consist of approximately three volumes of ether to one of tetrachloride. If the ether contains much water, a turbid solution may result upon mixing with the tetrachloride. In our work water-free ether was used.

As representative of another type of leather, a piece of chrome calf containing some sulphonated oil was analyzed. Extraction by the ether-tetrachloride mixture showed a fat content of 6.10 per cent., while the petrol extract showed only 4.85 per cent. Similar differences were obtained with numerous leathers, the petrol figure always being low. It was found that a partial separation of the fats in a leather could be effected by extracting first with petrol and then with ethyl ether.

In connection with this work we had occasion to try out the modified method of fat extraction proposed by Levi and Orthmann,[1] which is as follows:

[1] This JOURNAL, **10**, 445 (1915).

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"Place 10 grams of the finely divided leather into a 250 cc. bottle, add 200 cc. of petroleum ether, stopper the bottle well, and let digest 24 to 72 hours, according to the time allowed for reporting the result, during which time shake the bottle and contents frequently. Then withdraw 100 cc. and place into a tared dish or flask, evaporate the ether, dry and weigh in the usual manner, multiply the weight by 20 which gives the per cent. of fat."

From purely theoretical considerations one would expect this method to give lower results than the Soxhlet method, since some of the fats probably remain adsorbed by the leather. The comparative figures given by Levi and Orthmann show this to some extent, but are inconsistent in that, in a few cases, results are obtained which are actually a little higher than those obtained by the Soxhlet method. They mention having experienced difficulty in some cases of obtaining concordant results by the Soxhlet method. Although all of our leather analyses are made in duplicate, we have not experienced any difficulty in getting nearly identical results for the same sample. In order to illustrate this and at the same time to compare the two methods, we divided a well prepared sample of leather into six parts for determining the fat by each method in triplicate, using petroleum ether as the solvent. Table II shows the results.

TABLE II.—FAT EXTRACTIONS IN TRIPLICATE.

Levi-Orthmann method			Soxhlet method		
7.86	7.83	7.88	8.48	8.49	8.49
average, 7.86			average, 8.49		

Concordant results are readily obtained by either method, but the effect of adsorption is clearly shown by the difference between the average results. It should be noted in the Levi-Orthmann method that there is danger of losing some of the petrol by evaporation while the bottles are not stoppered. This may explain why they obtained results in some cases slightly higher than by the Soxhlet method. What has been said concerning the inferiority of petrol as a solvent holds also for the Levi-Orthmann method, but if ethyl ether were used in this method, the danger of getting high results through evaporation would naturally be increased.

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Summary and Discussion.

Petroleum ether is unsuitable for the estimation of fat in leather because it does not dissolve all of the fats.

Carbon tetrachloride is a better solvent than petrol, but its high boiling point requires that care be exercised in its use lest the leather itself be attacked. A portion of the leather used in preparing Table I was extracted for 8 hours with carbon tetrachloride, but the electric hot plate was regulated so that the solvent siphoned over about twelve times per hour. The fat determination showed 9.85 per cent., which is in agreement with the determination of 9.88 per cent. where the distillation was carried on at only half the rate. But, where the higher temperature was used, the extraction thimble was found to have been attacked (when dried, it could be crumpled to dust in the hand), the water-soluble matter in the leather rose to 7.10 per cent. and possessed a dark color and unpleasant odor not found in the other water extracts.

Ethyl ether is the best pure solvent examined, but it has the disadvantage of being very inflammable.

A mixture of equal volumes of ethyl ether and carbon tetrachloride was found to be fully as good a solvent as ether alone and to possess the advantage of not being readily inflammable. If a lighted match be held over some of the mixture in a watch glass, the ether will burn in periodic puffs as it leaves the mixture, but will not continue to burn when the match is removed.

The method proposed by Levi and Orthmann was found to give lower results than are obtained by the Soxhlet method.

We recommend that a committee be appointed to consider the advisability of substituting a mixture of ethyl ether and carbon tetrachloride for petroleum ether in the official method for the determination of fat in leather.

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AN EXTRACTOR FOR WATER-SOLUBLE IN LEATHER.

By Lloyd Balderston and W. K. Alsop.

Among desirable features for an extraction apparatus to be used in determining water soluble materials in leather are the six enumerated below.

1. Provision should be made for maintaining the extractor at the required temperature.
2. The apparatus should be so arranged that the leather sample will be covered with water during the extraction.
3. The flow of water through the sample should be capable of being regulated by means of a single stop cock.
4. There should be an independent water supply for each sample, so that continual watching to prevent flooding will not be necessary.
5. All parts should be easily accessible for washing, and the construction as simple as possible.
6. Alundum thimbles should be provided to hold the samples, that may be easily removed, and may be weighed after extraction.

The apparatus shown in the accompanying cuts has been designed with these qualifications in view. The sample is placed in the alundum thimble *a*, Fig. 2, fitting loosely in a copper cylinder *b*, which is soldered in place in a copper vessel *c* (Figs. 1 and 2), projecting a little at the top, to prevent water from accidentally running in. The copper flask *h* holds the water for extraction, a suitable quantity of water at 50° being placed in it when it is time for the percolation to begin, and the flask then inverted in the position shown. The rate of flow is now regulated by means of the screw pinch cock *e*. The vessel *c* is filled with water, heated to 50° by a large burner, which is then turned out, and the temperature maintained by a small burner controlled by a Roux gas regulator. It has been found unnecessary to use a gas regulator as the temperature is easily controlled to within a degree with the burner used to heat the water to the required temperature. After the percolation is started, the hood *d* is lowered so as to cover the flasks. Inside the hood is an incandescent lamp controlled by the switch *g* which serves to keep up the temperature of the water in the flasks. By choosing a suitable size of lamp, the temperature inside of the hood may be kept very close to 50°. The incandescent lamp feature, while con-

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venient is not really necessary as the required temperature is practically maintained without it and if not can be controlled by

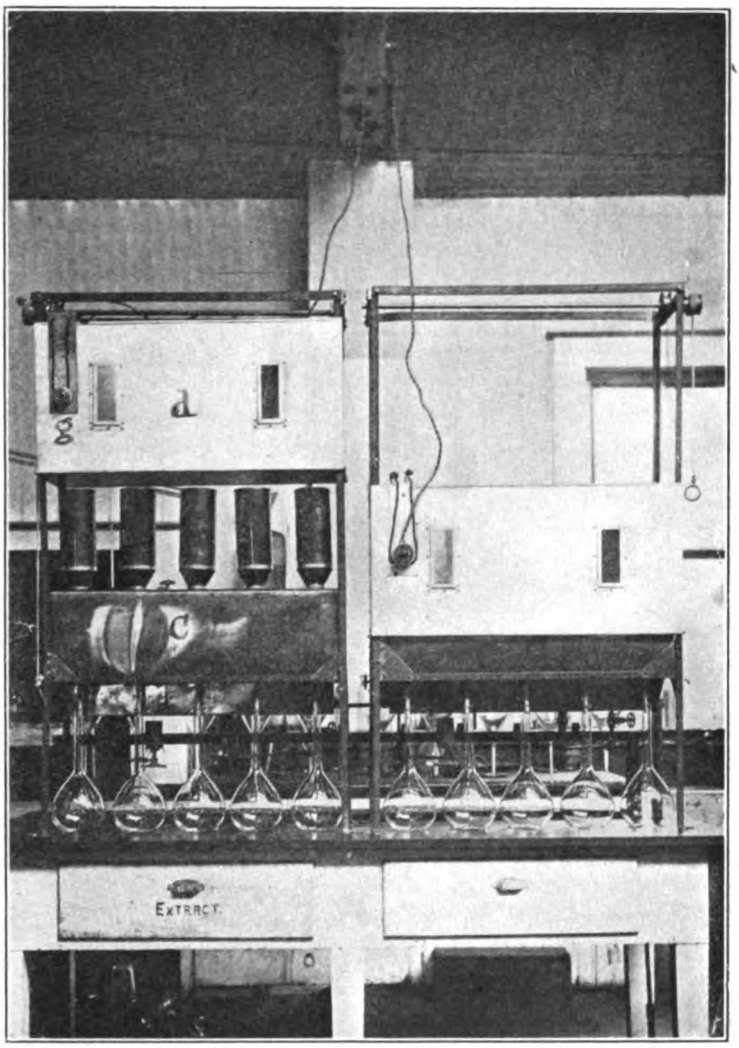

FIG. 1.

the temperature to which the water in the bath is heated. Fig. 1 shows two extractors, each holding five samples, one with hood up and one with it down. By making the tank a little wider it

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could be made to hold ten samples by having a row of five extractors on each side and the burner in the middle between them. The whole apparatus is supported on an angle-iron frame riveted together, and the tank *c* is at such a height as to permit a 2-liter flask to stand directly under the extraction cylinder, as shown.

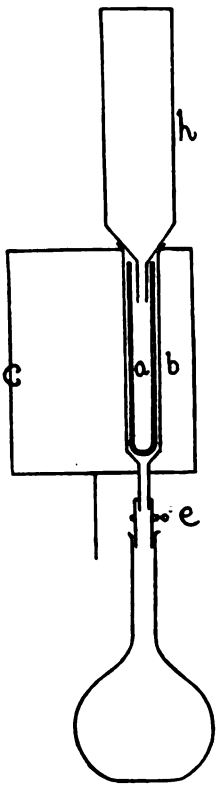

FIG. 2.

If twenty samples are ready to be analyzed, ten may be placed in the apparatus in the afternoon and left over night to digest cold. The other ten may be placed in their thimbles and stood in suitable cylinders over night. Next morning the apparatus is heated and the extract taken from the first batch in the morning hours. These thimbles are then withdrawn, and the other set placed, with the water in which the samples have been soaking, in the apparatus. Thus the twenty samples can be finished in one day.

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ACTIVATED SLUDGE AND THE TREATMENT OF PACKING HOUSE WASTES.*

By Langdon Pearse,

Division Engineer, in Charge Sewage Disposal Investigations, the Sanitary District of Chicago.

Introduction.

With the concentration of packing houses near or in large cities, the problem began of treatment to avoid nuisance. In Chicago this condition arose in the early 60's. In other localities the difficulties appear of more recent origin. Economies enforced by competition have now reduced the losses so that in the large houses every possible by-product is sought. However, organic material escapes with floor washings, paunch manure, etc., which is troublesome, both as suspended matter or in solution. In the treatment of these liquid wastes the activated sludge process appears particularly promising.

Raw Sewage.

The character of the raw sewage varies with the local conditions. The experiments of the sanitary district have been conducted on a mixed domestic and packing house sewage (Center Avenue sewage), containing by volume perhaps 25 per cent. of domestic sewage. The experiments of the packers have been conducted on the effluent from individual houses, containing considerably higher amounts of suspended matter as well as organic matter in solution (Table I).

Testing Work—General.

The early tests on packing house wastes were made at Fort Worth about 1901, on a strong sewage direct from the house. The devices tried included single story settling and septic tanks, intermittent sand filters and aeration. No direct record is available of the results, but the conclusions drawn by the packers point to odors, expense and large areas required for works.

In 1912, the sanitary district began a campaign for the treatment of industrial wastes and as part of the work, established a testing station in which were tried grit chambers, screen (fine and coarse), settling in single and two-story tanks, chemical pre-

* *American Journal of Public Health*, Jan., 1918.

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cipitation (both with alkali and acid), and sprinkling filters. The results were published[1] at a time when the activated sludge process was just being talked of. The testing work was therefore extended to cover the activated sludge process. Preliminary studies in cans 2 feet in diameter by 10 feet deep proved very encouraging. Larger scale experiments were begun early in 1916, and have been continued since. They have been successful in demonstrating the adaptability of the activated sludge process for handling packing house sewage mixed with domestic sewage.

TABLE I.—TYPICAL ANALYSES OF PACKING HOUSE SEWAGE. PARTS PER MILLION.

Source	Nitrogen as—				Oxy. Cons.	Chlorine	Suspended matter			Alkalinity
	Total org.	Free Amm.	Nitrites	Nitrates			Tot.	Vol.	Mixed	
Center Av.[1] day	79	22	0.49	3.04	268	1100	505	461	144	291
night	..	..	..	..	..	..	163	112	51	..
Halsted St.[2]	260	28	..	..	257	365	428	344	84	340
Ashland Av.[3] day	73	20	0.21	1.97	245	920	860	657	203	358
night	34	18	0.08	0.86	70	537	..	..	..	237
Armour & Co.[4]										
Hog house day	..	..	..	..	..	..	903	..	..	.
night	..	..	..	..	..	..	449	..	..	.
Swift & Co.[5] day	56	26	..	..	290	..	937	815	122	278
night	21	9	..	..	92	..	222	181	41	210
Wilson & Co.[6]	194	78	..	..	466	..	1040	990	50	395
Armour & Co.,[7] Fort Worth	..	..	..	..	.	..	3000	..	..	..

NOTE.—Chicago Analyses from Report Industrial Wastes, 1914 (1).

[1] Average, 1913.
[2] July 28, 1911, 4 hrs.
[3] Fourteen day samples, ten night samples, 1913.
[4] May 23 to 25, 1911.
[5] June 6 to 10, 1911.
[6] June 29 to July 1, 1911.
[7] Verbal statement of W. C. Moore, chemist, Armour & Co., Fort Worth.

TESTING STATION—THE SANITARY DISTRICT OF CHICAGO.

The activated sludge plant originally consisted of a rotary screen, four tanks in which the sewage is aerated, one tank for settling the aerated sewage, one sludge storage tank, two blowers with motors for supplying air, a sludge pump for returning the sludge to the aeration tanks from the settling tank, or the sludge storage tank, and a Venturi meter with recording apparatus for determining the quantity of air used.

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The rotary screen is of the Weand type, cylindrical in shape, 2 feet 4 inches diameter by 4 feet 8 inches long, covered with 30-mesh brass wire screen, supported on a ½-inch mesh screen. In the summer of 1917, the 30-mesh screen was replaced by a 20-mesh.

The four aeration tanks are each 6 by 23 feet in plan, 12 feet deep, inside dimensions, of 3-inch Oregon fir, well bolted together, with air distributors of filtros plates set in hopper bottoms of concrete faced with hollow tile. The plates are arranged differently in each pair of tanks. The ratio of plate area to tank area is approximately 1 to 6.3 in both the tanks with one row of plates down the center and those with the rows transverse to the length of the tank. After remodeling, the effective plate area was found to be 1 to 8. The capacity of each tank is about 11,000 gallons to the flow line. The tanks were first connected in series and provided with inlet and drain pipes, so that they can be operated separately on the fill-and-draw plan, as well as a whole with continuous flow. The air system is arranged with a main header to each tank, from which branch pipes feed each set of plates. Three small Venturi meters are provided to set on the main header lines in a by-pass to check up the flow of air to each tank.

The circular tank is 12 feet in diameter with 12-foot staves, built with a hopper bottom of the Dortmund type, originally with a slope of 0.6 vertical to 1 horizontal. The sewage enters the tank in the center near the bottom, the settled sewage passing off from the top around a peripheral weir. As the length of the weir is great and the sheet of water passing over proved very thin, "V" notches were cut in the crest to facilitate adjustment. The tank is provided with a sludge pipe for discharging the sludge onto the drying beds, and a suction pipe to the sludge pump.

An old circular Dortmund tank, 8 feet outside diameter, with 10-foot staves, has been fitted up as a sludge storage tank. It can also be used as a settling tank in connection with one of the aeration tanks.

Two rotary blowers of the Connersville make, Boston type, belt driven, supply the air for the plant, one with a capacity of 300 cubic feet per minute against a pressure of 6 pounds per

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square inch, driven by a 20 horse-power motor, the other with a capacity of 150 cubic feet per minute against a pressure of 10 pounds, driven by a 10 horse-power motor.

After considerable experiment, the settling tank was remodeled and the bottom hopper slope made 60° with the horizontal. A straight flow settling tank was also added, with steep hopper bottom slopes. Later the plant was changed again to permit of separate aeration of the sludge followed by settling before pumping the concentrated sludge back to mix with the incoming sewage. The period of aeration in contact with the sewage has been cut. The amount of air used is somewhat less than when the sludge was aerated entirely in contact with the sewage.

Summary of Activated Sludge Results.

The sanitary district experiments[2] on the activated sludge up to March, 1917, have shown that the following conditions must be met:

1. The sewage should be screened with a fine mesh screen. Thirty-mesh has been used. This removes from 600 to 1,000 pounds of dry material per 1,000,000 gallons of day flow.

2. The screened sewage can be aerated in continuous flow tanks using 4 cubic feet of air per gallon of sewage, with an 8-hour contact period of sewage and activated sludge. This will produce an effluent, practically stable in summer conditions.

3. Sufficient sludge storage capacity in the aeration tanks should be provided to care for at least 140 per cent. of the sewage entering the tanks. Actually from 40 to 80 per cent. of the incoming flow is returned from the settling tanks, as a mixture of sludge and sewage.

4. The depth of the tanks has been taken at 16.5 feet over the plates. The air distribution proposed is through filtros plates set in unit boxes of cast iron, the ratio of filtros plates to the superficial area of the tank is 1 to 6.

5. The system provides the following approximate recovery of solids:

Grease as scum 360 pounds per 1,000,000 gallons, as grease 47 pounds per 1,000,000 gallons.

Screenings 600 to 1,000 pounds of dry material per 1,000,000 gallons of flow.

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Sludge 2,000 to 3,000 pounds of dry material per 1,000,000 gallons.

Testing Work—Armour & Co., Swift & Co., Wilson & Co.

Armour & Co. have made an extensive study of the treatment of individual house effluents both on the hog house at Chicago[3] and on the combined outfall for Armour and Swift at Fort Worth.[4] The results sought have been largely from the standpoint of determining the availability of material recovered for fertilizer. The Chicago results approximate those of the sanitary district.

At Fort Worth, however, a very strong sewage has to be handled, because owing to the scarcity of water, waste is cut to a minimum. The trend of the experiments as judged from the published data[5] and a personal visit to Fort Worth, indicates that for the strong packing house waste at Fort Worth:

1. Preliminary screening is necessary. Thirty-two mesh wire screen has been used.
2. Preliminary sedimentation, accompanied by grease removal, is desirable.
3. Dilution of the strong sewage will facilitate treatment.
4. In the aeration of the sludge contact with the liquid, 35 per cent. sludge is desirable.
5. Re-aeration of sludge in a separate tank improves the sludge.
6. A stable effluent, well clarified, can be made.
7. The air consumption will be high, averaging from 6 to 9 cubic feet of air per gallon of sewage with a 10-hour period of contact.
8. The use of acid in de-watering the sludge coagulates the sludge both quickly and readily, reducing the moisture content below 85 per cent.

Wilson & Co. (when known as Sulzberger Sons Co.) ran a small testing plant on the effluent of part of the packing house. Quantitative data is not obtainable, but examination showed clarification accompanied by recovery of solids.

Swift & Co. have built an extensive experimental plant on a sewer containing typical concentrated packing house sewage.

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Although practically completed a year ago, the plant has not been operated to date, owing to press of war business.

Arrangement of Tanks.

The best arrangement of plant is not yet determined. Two schemes have been tried by the sanitary district, one in which the sludge is aerated entirely in contact with the sewage, the other in which the sludge and sewage are aerated for a short time, the settled sludge, however, being re-aerated and re-settled before return to the initial point. The latter arrangement has shown somewhat smaller requirements in the amount of air, and a reduced volume of sludge to be returned.

Stability of Effluent.

The amount of air noted in the experiments of the sanitary district (4 cubic feet per second per gallon of sewage) is apparently sufficient to produce a practically stable effluent in summer weather. In the winter, with the same amount of air, the effluent is of lower stability, when tested by incubation at room temperature. If a stable effluent is then required, 6 cubic feet or more of air per gallon of sewage may be needed, according to the temperatures of the sewage and air.

Mixed *vs.* Undiluted Wastes.

Although the evidence to date is not absolutely conclusive, the indications are that a mixed domestic and packing house sewage is more amenable to treatment than the strong packing house sewage. This indication is apparently confirmed by the results at Fort Worth.

Air Distribution.

The distribution of air appears at present to be best served by the use of filtros plates. Perforated pipes have been tried both at Chicago and Fort Worth. More air is required than with the filtros. The ratio of gross area of plate to tank area at Chicago was 1 to 6.3 with net area of 1 to 8. At Fort Worth 1 to 7 has been used.

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Baffling and Agitation. Tank Design.

Considerable study is required on both domestic and industrial sewage to determine the best design of tanks. In this connection the design of the bottom of the aeration tanks deserves attention. In England, Jones and Attwood have worked out a saw tooth design.[5] In the United States, Nordell at Milwaukee has worked out a design with a curved bottom, the plates being placed eccentric to the center of the tank.[6] At the Chicago testing station simple baffling has been tried, with different arrangements of shallow hoppers in the bottom. No directly comparable results are available.

Sludge Settling.

Following aeration of the mixed sludge and sewage, the sludge is settled out. The experience of the sanitary district indicates that the period may be short, ½ to 1 hour, and that the bottom slopes of hopper bottom tanks should be about 60° with the horizontal. Velocities should be low. The sludge may be removed continuously by air lift or centrifugal pump. Flat slopes around 45° or lower appear to encourage "hanging" and consequent septic conditions. A straight flow settling tank worked.

The required settling period, however, depends vitally on the condition of the sludge and may vary also with the season of the year.

Sludge Treatment.

The handling of the sludge is probably the most knotty problem of all. In the sanitary district work, with screened sewage, exclusive of screenings, about 46,500 gallons of liquid sludge containing 99.2 per cent. water accumulated per 1,000,000 gallons of sewage over a period of 9 months. This is equivalent to 2,420 pounds of dry solid per 1,000,000 gallons. The amount of dry solids per 1,000,000 gallons appear to vary between 1,100 and 4,500 pounds exclusive of screenings. The screenings caught on a 30-mesh screen will vary from 500 to 1,200 pounds of dry material per 1,000,000 gallons of day flow. During a period of 6.5 months the reduction of suspended matter was 2,820 pounds as against a sludge removal of 2,680 pounds of dry material per 1,000,000 gallons.

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The essential point is to remove the water. Various expedients have been tried, which may roughly be sub-divided into (1) settling, (2) the use of coagulants, including both alkali and acid, (3) filter pressing. Centrifuging has not yet been tried at Chicago.

With very liquid sludge, direct filter pressing is difficult, owing to the large amount of liquid to be handled. Preliminary treatment by settling with or without acidification is very helpful. Quiescent settling from 3 to 6 hours will reduce the moisture content to 98 or 98.5 per cent. The addition of about 6 pounds of sulphuric acid per 1,000 gallons of sludge (containing 98 per cent. moisture) seems to aid in filter pressing, and makes a sludge which leaves the cloths cleaner. A 2.5-hour pressing with acid treated sludge is equivalent to 3½ to 4-hour pressing with settled sludge. Moreover, acid treated sludge apparently keeps better and shows a somewhat higher nitrogen content.

The effect of acid on activated sludge is not at all the same in different places. Apparently on the sanitary district sludge, the effect of acid is a minimum, whereas at Fort Worth, on packing house activated sludge, the addition of acid produces a rapid coagulation, with immediate flotation of the sludge, the moisture content being quickly reduced. The water used in the packing houses there is very high in alkali. The sludge can be further reduced by drainage and retreating to about 85 per cent. moisture or lower. This phenomena does not appear at Chicago. Furthermore, it is estimated at Fort Worth that about 11,000 pounds of dry material can be recovered per 1,000,000 gallons.

Plain settling has considerable value in reducing the moisture content. However, the effectiveness is conditioned on the condition of the sludge. The settling is not as marked as on domestic sewage at Milwaukee or on packing house sewage at Fort Worth.

Filter pressing has been tried by the sanitary district on a small "Simplex" press, with plates 15 by 15 inches square, loaned by the Simplex Ejector Co., and demonstrated by Mr. Buckley. This press was the one used at Milwaukee, the results there being described in reference 6, with the addition of six radial ribs on each plate. The plates in the press have perforated steel strainer plates over the corrugations. Cakes from ½ to 1⅞ inches have been made in from 2 to 4 hours pressing, with pressures varying

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from 20 to 150 pounds, according to the character of the sludge and the preparatory treatment. Occasional steaming helped in keeping the cloths clean. The moisture content of the cake was varied, in general being around 80 per cent.

Sludge Analyses.

There appears to be considerable fertilizer value in activated sludge. Analyses show a high nitrogen content, compared to the screenings (Table II). Occasional analyses show press cake, particularly with acidified sludge, running from 5 to 6 per cent. of nitrogen on the dry basis.

TABLE II.—Typical Analyses of Screenings and Sludge, the Sanitary District of Chicago.

Source	Per cent. moisture	Calculated to dry weight			Ether soluble		Remarks
		Fixed	Volatile	Org. N.		Acidified	
Screenings	80.7[1]	4.7	95.3	2.18	5.9	9.4	Average 3 mos.
Sludge	99.15	37.4	62.6	4.17	6.00	9.25	Average 9 mos.

[1] Moisture content average of 9 months.

Screening.

The value of fine screening as a treatment preliminary to aeration is worth consideration. Our experiments show that a 30-mesh screen will remove from 500 to 1,200 pounds of dry material per 1,000,000 gallons of day flow. The screenings contain about 80 per cent. moisture after natural drainage. The nitrogen content is low, equivalent perhaps to barnyard manure (Table II). The material is largely paunch manure. The material removed is the coarser suspended matter, consequently the amount of depositing material is lessened, which may tend to collect in the depressions of the aeration tanks. From the operating standpoint the removal of this material by screens seems desirable, as it is largely inert, of vegetable origin and slow to decompose. From the standpoint of handling the sludge, however, when the screen is running the sludge is somewhat harder to press. The screenings seem to act as a fibrous binder which aids pressing.

Recoveries.

The general indications at Chicago are (Ref. 2, p. 27-27) that grease and fertilizer may be recovered. The grease may be worth

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about 4 and 7 cents a pound at normal and war prices. The activated sludge, dried, if containing regularly 5 per cent. of ammonia may be worth about $12 per ton dry, under normal conditions, or possibly $18 per ton under present war conditions.

Odors.

The activated sludge testing plant operated at Fort Worth, at Chicago by Armour & Co. and by Sulzberger & Co., and by the sanitary district have been remarkably free from odor. The sewage tested in all cases has been fresh.

Costs.

The exact costs of plants for handling packing house wastes have still to be determined. Approximate estimates made by W. D. Richardson and the author for the conditions in Chicago[2] are subject to revision as better data is obtained, particularly in the costs of handling the sludge. As yet no large scale plant has been operated as a complete unit. For the 50,000,000-gallon daily plant, the first cost, exclusive of land, was estimated at $3,752,000. The annual cost, including interest, depreciation, and operating charges was estimated at $822,000, of which $270,000 was for electric power. The power was figured on a sliding scale which averaged about 0.7 cents per kilowatt hour. Including power the annual operating charge was estimated at $455,700.

Recoveries are uncertain in both value received and amounts. However, at normal prices an income of $150,000 to $300,000 may result, and at war prices $250,000 to $450,000, depending on the quality and quantity of material recovered. These results will help reduce the gross annual cost given above.

Further Developments.

Further development in the activated sludge process appears to be along the lines of reducing the amount of air used, improvement of settling tanks, and the more rapid reduction of water content of the sludge. Such development will tend to reduce both construction cost and operating charges.

The reduction in the use of air may be obtained along the lines of development in the design of tanks, to promote mixing

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and distribution of air, and possibly along the line suggested in England of intermittent application of air.

The improvement of settling tanks is in a transition stage. The steep hopper bottomed tanks are effective. However, other devices may be workable, such as the Dorr tank, particularly where the returned sludge is re-aerated separately and re-settled before return to the inlet.

Ways and means of reducing more rapidly the water content of the sludge should be studied, either in preparation for filter pressing or as a direct preliminary to drying. This is a complex problem, verging on the domain of physical chemistry.

Conclusion.

The activated sludge process offers the best promise of a solution of the problem of treating packing house waste of any suggested up to the present time. For the study of conditions in Chicago the construction of a unit plant has been recommended to handle 1,500,000 gallons per 24 hours, to obtain working results on a large enough scale to determine the design of the final plant.

In conclusion the writer wishes to acknowledge the courtesy of the chief engineer of the sanitary district of Chicago, Mr. George M. Wisner, for the use of information, and the assistance of Mr. J. J. Newman, assistant engineer, who has charge of the experimental work under the author's direction.

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4. "Marked Advance in Treating Sewage from Packing Houses." G. B. Zimmele, *Eng. News Record*, 78, 436, 1917.
5. "Sewage Treatment, Worcester, England," Booklet No. 52. Jones & Atwood, Ltd.
6. Sewerage Commission of the City of Milwaukee, 1916.

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ANALYSIS OF VEGETABLE SOLE LEATHER.*

The analysis must be done in complete duplicate and the average reported. Where the sample supplied is insufficient for this purpose, or if in any case the two results differ by more than 1 per cent. on the sample and for some reason a re-determination is impossible, a note to this effect must be included in the report.

Preparation of the Sample.—The sample must be finely divided (with a spoke-shave or similar tool) into pieces sufficiently small to pass into the mill or cutting machine used, so that the sample taken for the determination of the original moisture may represent a fair average.

Original Moisture.—Five grams (or more) of the well-mixed shavings are dried in the vacuum oven at 98°-100° C., for 2 hours, or to constant weight in a water oven, and weighed in a covered vessel.

The remainder of the sample or a fair representative part is ground to a fine fluffy powder or where impossible to grind is shaved to a thickness of about 0.5 millimeter and the whole thoroughly mixed. The sample so prepared is used for the following determinations:

Moisture Determination for Calculation of Results to 14 Per cent.—Five grams are weighed into a basin or similar receptacle and dried and weighed as prescribed under "Original Moisture."

Total Ash.—Five grams are ignited in a platinum, thin porcelain or fused silica basin, at a very low red heat with occasional stirring with a platinum wire till a quite white ash is obtained. If this does not occur rapidly or if there is reason to suspect fusible salts, the charred mass must be crushed finely and washed on a small quantitative filter with 15-25 cc. of distilled water, the filter and charred mass returned to the original basin, dried and ignited completely. The wash water is added to the residue in the basin, evaporated and the whole again slightly ignited, cooled and weighed.

Determination of Oils and Fats.—Twenty-five grams are placed in a large Soxhlet, lightly packed, and extracted with

*** This method has been agreed upon by leading English leather chemists. The method was published in the February issue of the *Journal of the Society of Leather Trades Chemists*, galley proof of which was kindly sent us by the editor.**

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petroleum ether, boiling point 40°-60° C., for 6 hours on the water bath heated so as to produce regular syphoning. The solvent is distilled off the fatty residue which is dried in the vacuum oven at 98°-100° C. for 2 hours, cooled in a desiccator, and weighed.

Determination of Water Soluble.—The fat-free leather is spread on a plate in a warm place till the solvent has evaporated and is then transferred to a Procter extractor (omitting the sand), covered with water and allowed to stand over night. Next day the extractor is heated to 45° C. and the sample percolated with water at the same temperature to 1 liter in the course of 3 hours, the extractor not being stirred or allowed to run dry, but filled up with the warmed water as required, while the rate of flow is regulated by a pinch-cock to about 5.5 cc. per minute. The solution is cooled to 15° C., filled to the mark and filtered clear through any good quantitative filter, the first 200 cc. being reserved for sugar determination or rejected.

Total Soluble.—Fifty cc. (or preferably 100 cc.) of the filtered solution are evaporated to dryness on the water bath and dried in the vacuum oven for 2 hours and the result entered as "Total Soluble."

Soluble Ash.—It is necessary to use platinum, fused silica or thin porcelain dishes for the above determination, and the dry residue is treated as described under "Total Ash." If the soluble ash does not exceed 1.5 per cent., its further analysis is unnecessary.

Insoluble Ash is obtained by deducting "Soluble Ash" from "Total Ash."

Determination of Nitrogen.

Reagents.

Standard Acid Solution.—Fifth-normal hydrochloric or sulphuric acid.

Standard Alkali Solution.—Fifth-normal caustic soda.

Sulphuric Acid.—Specific gravity 1.84—pure for analysis.

Strong Caustic Soda Solution.—Three hundred and fifty grams in 1 liter.

Potassium or Sodium Sulphate.—Finely ground.

Indicator.—Methyl orange, or preferably carminic acid.

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Place about 0.7 gram (not exceeding 1 gram) of leather in a round-bottomed Kjeldahl flask. Add 8 grams potassium or sodium sulphate, and 20 cc. pure sulphuric acid. Heat over a low flame for about 15 minutes till frothing subsides, place a loosely fitting pear-shaped stopper in the neck of the flask, increase the heat till the mixture boils gently and continue (usually for 4 to 5 hours) till the solution is water white or at the very worst a faint greenish-yellow color, probably due to traces of iron. If the boiling has been too rapid the addition of 5-10 cc. of sulphuric acid is sometimes necessary to replace evaporation. In this case a corresponding addition of soda is required for neutralization. When cool, dilute with water and transfer to a distillation flask, connect with a condenser and run in 100 cc. of the strong soda solution through a tapped funnel. Distil with a good spray trap and preferably with the aid of steam, and collect the condensate in 50 cc. of fifth-normal acid. Titrate back with standard alkali.

cc. N/5 acid used $\times$ 1.573 = per cent. hide substance.

A blank test of the reagents is made with 1 gram of sugar.

Glucose.—To 200 cc. of the water-soluble extract add 20 cc. basic lead acetate, shake occasionally during 15 minutes, filter through an 18½-centimeter folded filter and to 110 cc. of the filtrate add 10 cc. saturated solution of sodium sulphate. Filter through a 15-centimeter folded filter (No. 5 Whatman is suitable). All but the last trace of lead is removed by this procedure. To completely accomplish this add a very small quantity of dry sodium carbonate (about 0.1 gram) and filter once more. Pipette 50 cc. of the slightly alkaline filtrate into a small flask, moisten a thin strip of blue litmus paper and place it at the bottom of the neck of the flask. Add hydrochloric acid (specific gravity 1.125—24.8 per cent. HCl) drop by drop, testing with the litmus paper each time, 2 to 5 drops will be required to make the solution just acid, and then add 5 cc. in excess. Heat in the boiling water bath for 2 hours under a reflux condenser, remove and neutralize with strong caustic soda solution (about 350 grams in 1 liter) the equivalent of which has been previously determined by titration against 5 cc. of the HCl and a drop of methyl orange in 50 cc. water. Cool, transfer to a 100 cc. grad-

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uated flask and make up to the mark. Fifty cc. are used for the determination of reducing sugars by the A. L. C. A. method, using Munson and Walker's tables. See the A. L. C. A. annual booklet of methods.

Milligrams glucose $\times$ 0.192 = per cent. glucose in leather.

A blank experiment must be made with the reagents employed, and any copper found must be deducted from that found in analysis before calculating glucose.

The following method of reporting is recommended:

		Per cent.
Moisture of sample as received —— per cent.		
Moisture calculated as		14.0
Oil and fat		——
Soluble in water at 45° C.....		——
Ash of soluble salts.....	——	
Glucoses	——	
Other organic matter	——	
Insoluble leather substance		——
Hide substance by Kjeldahl.....	——	
Fixed tanning matters	——	
Ash of insolubles	——	
		100.0

(Fixed tanning matters obtained by difference.)

SUGGESTIONS ON SOME COMMON PRECIPITATIONS.*

By George H. Brother.

A number of my friends engaged in analytical work have spoken to me about filtration difficulties they have encountered in some of the most common determinations. According to their statements, they are unable to get filters which will "hold" unless they resort to the very retentive, but comparatively slow papers. After considerable investigation of the subject, I have come to the conclusion that their blame is largely misplaced. The fault, in the great majority of cases, lies not so much in the paper used as in the method of precipitation. For this reason I am giving a few "tricks of the trade" which, I am sure, will be helpful to any analyst not already acquainted with them, if used in standard

* *J. I. and E. C.*, Feb., 1918.

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methods given in any reputable reference, such as Treadwell-Hall.

Barium Sulphate.

The sulphate solution should be about 200 cc. in volume and weakly acid with hydrochloric acid (1 cc. 1.2 specific gravity to a neutral solution). It should be heated to a temperature just below boiling,[1] and about half of the solution of barium chloride necessary for excess added drop by drop, stirring well meanwhile, and allowed to digest for about 5 minutes. The remainder of the precipitant is then added (not necessarily so slowly, though the solution should be stirred during the addition) and it is allowed to digest 10 or 15 minutes longer. It is then ready for filtration.

A precipitate formed in this way will be found quite crystalline and will be readily retained by a paper of moderately close texture. I have quite satisfactorily used Whatman 40, C. S. & S. 589 "White Ribbon," and Munktell's 0 instead of the slower Whatman 42, C. S. & S. 589 "Blue Ribbon," or Munktell's 00. In this way time may be saved in the filtration as well as in the much shorter period of digestion.

Calcium Oxalate.

Heat the solution of the calcium salt to just below boiling. Add excess ammonium oxalate solution, then just enough hydrochloric acid (specific gravity 1.2) to dissolve the precipitate. Add ammonium hydroxide solution drop by drop until distinctly ammoniacal, then run in a good excess. Digest at a temperature just below boiling for about ½ hour. Filter while hot and wash precipitate with hot water.

The important point in this determination is the acid oxalate solution from which calcium oxalate is precipitated by the addition of ammonia. The formation of calcium hydroxide is in this way prevented and a crystalline precipitate of the oxalate insured. The method works out the same if the original calcium solution is made acid, the ammonium oxalate (or oxalic acid) added, then the ammonium hydroxide solution, as above. The objection to

[1] "Just below boiling" gives all the advantages of precipitation and digestion in hot solution and eliminates the risk of superheating and loss through frothing or bumping.

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this procedure is, of course, the absence of an indicator to prevent the addition of an unnecessary excess of acid. For volumetric lime determinations, where an ashless paper is an unnecessary extravagance, Whatman 3 and 30 or Munktell 100 will be found quite satisfactory if the precipitation is done by this method.

Ammonium Phosphomolybdate.

The principal difficulty with this precipitation is the adherence of many analysts to the old rule, *viz.*, heat the phosphate solution to about 70° C., precipitate and digest at no higher temperature. If this procedure is followed, digestion for several days is necessary to secure a filterable precipitate, and even then success is uncertain. I have found the method of Woy with modifications, as given in Treadwell-Hall's "Quantitative Analysis" (1915), p. 437, to be very satisfactory. The essential point of this method is precipitation and digestion at a temperature just below boiling. The phosphate solution should be made distinctly alkaline with ammonium hydroxide, then nitric acid added to slight excess. This is a convenient way to insure the presence of ammonium nitrate in the solution and prevents the addition of too great an excess of nitric acid. It should be heated to boiling, then, while stirring, add the ammonium molybdate solution drop by drop from a pipette. Digest on a hot plate at a temperature just below boiling until the supernatant liquid is clear and colorless (usually about 15 minutes). Decant, wash and filter as usual. Occasionally when the precipitant is added, no precipitate immediately forms, but instead the solution becomes colored yellow. Digestion, as described above, will bring about complete precipitation and conversion of the yellow solution to colorless, but in such cases more than 15 minutes' digestion is usually required. The precipitate thrown down in this way is coarse enough to be retained by quite open-textured papers, such as Whatman 1 and 31, C. S. & S. 595, or Munktell's OB.

Magnesium Ammonium Phosphate.

Here, again, I think the difficulty lies in the use of old methods, which called for the addition of magnesia mixture to an *ammoniacal* solution of the phosphate *in the cold*. The method of B.

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Schmitz, as outlined in Treadwell-Hall (*Loc. cit.*), p. 434, gives much more satisfactory results. The phosphate solution is treated with excess magnesia mixture solution, hydrochloric acid added just to dissolve the precipitate and it is heated to boiling. Ammonium hydroxide solution is added slowly until a crystalline precipitate forms. If the precipitate is not crystalline, it should be redissolved by the addition of hydrochloric acid and reprecipitated with ammonia. When a distinctly crystalline precipitate has formed, the solution is made ammoniacal, it is removed from the hot plate and allowed to cool. When cold, add a volume of ammonia (specific gravity 0.9) equivalent to about one-fifth the volume of the solution, and at the end of about 10 minutes it is ready to filter.

The reverse of these determinations, *i. e.*, the determination of magnesium by precipitating with a soluble phosphate, are carried out analogously. A number of chemists in brass work are having trouble with filtering tin dioxide. I have undertaken to investigate this determination, and hope to have some results on it before long.

SOAP AND ITS USE IN FAT-LIQUORS FOR LEATHER.*

By A. Harvey.

Before considering the value of soap for fat-liquoring purposes, it will be as well if the preparation and properties of soap be first dealt with.

The making of soap is essentially a chemical process, and depends upon the fact that alkalies such as soda and potash will decompose "fixed oils," such as cottonseed, cocoanut, tallow, cod, and palm oils, with the production of a soap, together with the liberation of glycerol. The process is termed saponification, and may be illustrated by the following chemical equation, bearing in mind that the "fixed" fats and oils may be spoken of as glycerides of fatty acids:

$$C_3H\begin{cases}COOC_{17}H_{35}\\COOC_{17}H_{35}\\COOC_{17}H_{35}\end{cases} + 3KOH = C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3(C_{17}H_{35}COOK)$$

Fat + Potash = Glycerol + Soft Soap

* *The Leather World*, Jan., 1918.

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When such fats or oils are saponified with potash, the resultant soap is a "soft" soap, whereas the "hard" soaps are produced as the result of saponification with soda.

Mineral oils cannot be saponified like the "fixed" oils or glycerides. This is due to the difference in chemical composition. The mineral oils are hydrocarbons, *i. e.*, contain only carbon and hydrogen.

With regard to resin, which is sometimes used for making soaps, especially the cheaper kinds, this is the residue left in retorts after the distillation of turpentine. It is not saponifiable in the true sense of the term, but as it possesses acid properties, due to abietic acid, it may be neutralized with soda or potash to produce a substance having some of the properties of soap. As explained above, a certain quantity of glycerol (glycerin) is liberated or set free during the saponification process. On a large scale, such as in the ordinary soap factory, the liquors containing the glycerol are purified and concentrated in vacuo in order to obtain the pure glycerine of commerce. Unfortunately, in the preparation of soft soap, much of the glycerine is lost. At the present time, however, a large quantity of soap is made directly from the fatty acids themselves by a process of neutralization. To obtain these fatty acids, the fats or oils are submitted to a splitting process whereby they are changed in fatty acids and glycerine. The glycerine so obtained does not require such an elaborate purification as does that obtained from the ordinary saponification process.

The neutralization of fatty acids by alkalies to form soaps may be illustrated by the following chemical equation, taking as an example stearic acid:

$$\underset{\text{Stearic Acid}}{C_{17}H_{35}COOH} + \underset{\text{Caustic Soda}}{NaOH} = \underset{\text{Sodium Stearate (Hard Soap)}}{C_{17}H_{35}COONa} + \underset{\text{Water}}{H_2O}$$

Thus two ways of making soap are available, and both may be utilized by the leather manufacturer for making soap on a small scale. It might be added that the advantages of making one's own soap are many: the quality is always the same, and a certain amount of economy can also be effected.

It is usual for fat-liquoring purposes to use soft soap, so that the only alkali required is potash. At the present time, however,

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potash is somewhat scarce and expensive, and might be partly substituted by soda, but not wholly.

The quantity of alkali necessary to completely saponify a given weight of an oil may be ascertained from the analytical figure known as the "saponification value." This number is the quantity of potash in milligrams required to saponify 1 gram of the oil. In the following table are given the saponification value of some of the more common oils, together with the quantities of soda (for hard soaps) and potash (for soft soaps) required to saponify 10 pounds of the oil:

Oil	Sap. value	Soda NaOH Pounds	Potash KOH Pounds
Cocoanut oil	257	1.83	2.57
Tallow	195	1.39	1.95
Cottonseed oil	193	1.37	1.93
Sesame oil	192	1.36	1.92
Bone fat	190	1.35	1.9
Castor oil	180	1.28	1.8
Arachis oil (peanut)	193	1.37	1.93
Linseed oil	190	1.35	1.90
Neats-foot oil	195	1.39	1.95
Soya bean oil	192	1.36	1.92

As a general rule the quantity of soda (caustic soda) required may be obtained by multiplying the quantity of potash by the factor 0.713.

For the preparation of soap by saponification, the oil is weighed out and heated in a steam-jacketed pan, and the alkali, previously dissolved in as small a quantity of water as possible, added with constant stirring of the mixture. Saponification will soon be complete, and the mass will set solid, or nearly so, even in the case of soft soaps. This is due to the absence of the large amount of moisture which is usually present in commercial soft soaps. As a matter of fact, 1 pound of soft soap prepared as above will be equivalent to about 1½ pounds of ordinary soft soap.

When preparing soap from fatty acids by neutralization, the alkaline carbonates may be used instead of the more expensive caustic alkalies. The quantity required must be first ascertained from an estimation of the acid value of the fatty acids. When adding the alkali liquor to the hot fatty acids, care must be taken, or the mixture will froth considerably, due to the evolu-

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tion of carbon dioxide gas. When using carbonates for neutralizing, the reaction can be expressed by the following equation, taking stearic acid again as an example:

$$2C_{17}H_{35}COOH + Na_2CO_3 = 2C_{17}H_{35}COONa + CO_2 + H_2O$$

Stearic Acid + Soda Carb. = Hard Soap + Carb. Dioxide + Water.

So far only the preparation of soap has been considered; the next thing is the properties of various soaps. Soaps should dissolve readily in hot water, and the potash or soft soaps are more soluble than the hard or soda soaps. The properties of a soap depend also upon the nature of the fatty acids from which it is made.

Soap made from castor oil is very soluble in water, more so than many others, and the soda or hard castor oil soap is a good substitute for a non-potassic soap. This is due to the low solidifying point of the fatty acids of this particular oil.

Cottonseed oil is used in cases where soft soap with the characteristic "fig" is required, although it cannot be said that "figged" soaps have any advantage over non-"figged" for fat-liquoring purposes. The figging is probably due to the separation of the potash salts of some of the fatty acids having a high solidifying point, *i. e.*, partial crystallization of the soap.

For many reasons, which cannot be entered into at the present moment, one of the best soft soaps may be made from linseed oil.

When using salted egg yolk as a constituent of a fat-liquor in conjunction with a hard soap, one made from cocoanut or palm nut oil is to be recommended for the following reason: The salt in the egg yolk is liable to precipitate some of the soap in the form of a curd, due to the insolubility of the hard soaps in salt solution. The hard soaps from the two oils mentioned above are exceptions to this general rule, hence the reason why they should be used in the presence of salted yolk. It will not be of much service to give the quantities of other soaps for fat-liquoring purposes, as it seems probable to the present writer that the stability or otherwise of an oil soap emulsion is to a large extent dependent upon the method of emulsification, which resolves itself into an engineering question. Still, much information can be gained by the leather dresser by making a few experiments, using pure soaps prepared as stated above.

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ABSTRACTS.

On the Conservation of Skin by Desiccation. Ed. Nihoul. *J. S. L. T. C.*, Jan., 1918. In the October number of the *J. S. L. T. C.*, Mr. A. Seymour-Jones has called attention to the probability in the future of a deficiency of raw skins. It is therefore especially important to improve throughout the conditions of cure so as to ensure a minimum loss of hide substance.

Though cure by drying has always been in use, and will be increasingly important in remote districts without salt and with difficulties of carriage, it has always been disliked by the tanner, principally from the difficulty of judging quality, and the danger of conveyance of anthrax. Some believe that injury to the skin is due to the sun; others blame both this and humidity. On the other hand, Seymour-Jones and Abt consider that solar light and heat destroy anthrax and do not favor the production of spores.

It does not seem impossible to avoid condensation of moisture on the grain, by raising the skins above the ground, so as to expose both sides to draughts of air and by avoiding drying over ground covered with vegetation, which is necessarily cool and damp. Hann states that in tropical countries dry ground may reach temperatures of 75°-85° C., so it should not be difficult to dry sufficiently rapidly to prevent putrefaction, if the skins are not tainted before exposure. Putrefaction cannot fully set in till the tissue is completely dead, and the skin cells retain vitality for some time after flaying. Dr. Carrel has maintained life for months in fragments of tissue artificially supplied with nourishment within certain limits of temperature, and the cells in the skin are for some time under these conditions.

The author next considers the direct effect of the sun's light and heat. The visible light comprises radiations of wave-lengths varying from 700$\mu\mu$ in the extreme red to 400$\mu\mu$ in the extreme violet, but beyond these at either end are invisible rays of longer or of shorter wave-lengths which the eye cannot perceive. All these radiations when absorbed may be converted into heat, those at the red end being most powerful in this respect, while the violet and ultra-violet have usually the greater effect in causing chemical change. When a series of waves falls on anything capable of vibrating in harmony, it sets it in motion, as a note sung will set in motion the corresponding wire of a piano, and the shorter waves thus harmonize with the periods of vibration of certain atoms and molecules, and induce such violent oscillations as in many cases to overcome the chemical attractions which unite them and lead to decomposition or rearrangement. As regards the heat effect, experiments on monkeys at Manila have shown that they are killed in one or two hours if quite unprotected from the direct rays of the sun, but if the head alone were exposed the animals remain well, although the temperature of the hair itself reach 47° C. (very much above blood heat) and no change took place in the skin tissues. The temperature in man does not rise nearly so much, owing to the greater

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development of the sudoriferous glands, but 37.4° was observed on Malays. In white men the temperature rises to a less extent but more rapidly, acting on the nerve-extremities in the skin, and causing there an increased flow of blood and a consequent rise in its temperature. They are also from the whiteness of the skin more exposed to the chemical action of the radiation.

Another effect of chemical action mentioned by Gibbs is the transformation of oxyhaemoglobin to methaemoglobin. This latter is a product of oxidation and the reaction is not reversible, but the body is further decomposed by ultra-violet rays into hematine and albumin. This to a large extent is prevented by the pigmentation of the skin of black races, and still more by the hair on hides.

Once the tissue is dead, the bacterial activity has free play and the enzymes specially attack the labile tautomeric substances which transform calorific into chemical energies. The propagation of the bacterial organisms themselves is however limited by temperature, each species having an *optimum* temperature of growth. For most of them, the temperatures reached in tropical sunshine are too high, and to many the effects of light are fatal. In the living tisues enzyme-actions proceed analogous to those produced by bacteria, but usually in opposite sense, building up rather than hydrolyzing and breaking down.

Besides the effect of heat just noted, more direct effects occur, such as coagulation of albumin and increased viscosity or hardening of tissues preventing the propagation of bacteria. These occur principally on the surface also checking the ready escape of moisture and allowing the moist interior to reach high temperatures, but the author is of the opinion that in absence of ammonia which facilitates the change, there can hardly be sufficient to change the fibrous structure into gelatine, and he considers the changes which lead to holes and blisters rather due to incipient putrefaction and the formation of bacterial zooglea.

As regards direct chemical action of the light, the rays of short wavelengths (violet and ultra-violet) are the most active and affect many organic substances, and especially those which rotate polarized light, and which usually are capable of change between ketonic and enolic forms, and this is specially the case with the proteid constituents of skin. Many bacteria are thus almost instantly killed by the ultra-violet radiations of the mercury vapour lamp. The ultra-violet rays are also capable of producing ozone, hydrogen peroxide and nitrous acid which have marked bacteriocidal powers and may penetrate the skin to parts which the direct rays cannot touch.

Sodium Sulphate (Glauber Salts) in Leather. THOMAS MANN. *J. S. L. T. C.*, Jan., 1918. Suggestion by the British Government to fix a limit for sodium sulphate in leather has caused the author to question what object is gained by this limitation. He decides that the presence of other sodium salts is just as harmful and that the quantity of such alkali bases should be determined. The usual method of determining sodium sulphate

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by calculating from the sulphuric anhydride is open to many objections. He suggests a method of determining all the sodium oxide present and figuring this to a sodium sulphate basis. This method consists of ashing a definite quantity of leather, treating the ash with an excess of sulphuric acid, which excess is driven off by heat and the ash again weighed. Barium sulphate, silica, sulphuric anhydride, and the oxides of iron, aluminum, calcium and magnesium are carefully determined and the sum of these deducted from the percentage of ash after treating with sulphuric acid. The balance is taken to be sodium oxide and is calculated to glauber salts.

The Distillation of Wood. J. C. LAWRENCE. *J. S. C. I.*, Jan., 1918. The author in a lengthy article gives a very complete description of the history and methods used in the distillation of wood, together with the yields obtained from different wood and the influences which affect such yields.

A New Reagent for Phloroglucinol and Catechol. M. JOACHIMOWITZ. *Biochem. Zeitsch.*, 1917, 324-358; from *J. S. L. T. C.*, Jan., 1918. p-Dimethylaminobenzaldehyde dissolved in sulphuric acid is a reagent for phloroglucinol, and gives a quicker and more localized reaction than Lindt's reagent. It was applied (microchemically) to the investigation of 464 different plants to determine the distribution of substances giving a coloration with it. Catechol gives the same reaction with this reagent and investigation reveals the fact that in many cases the coloration produced is due, at any rate partly, to this substance.

The Analysis of Oils. F. ERBAN. *Seifens. Zeit.*, 1916, 969; abst. in *Coll.*, 1917, 285; from *J. S. L. T. C.*, Jan., 1918. The usual method of determining neutral fat in soaps, turkey red oils, etc., is to shake out the weakly alkaline solution with ether or petrol ether. In order to avoid the solution of soap, and a consequently too high figure for neutral fat, it is best to shake out the ethereal solution with dilute hydrochloric acid. The small amount of fatty acid thus present in the ethereal solution can be recognized by its acid value, and its amount determined.

Detection of Fish Oils in Mixtures. T. MARCUSSON and H. V. HUBER. *Mitteilung des kgl. Materialprufungsamtes Gross-Lichterfelde*, 34, 56; abst. in *Coll.*, 1917, 285; from *J. S. L. T. C.*, Jan., 1918. The octabromide determination, up to the present regarded as reliable, cannot be used with deodorized fish oils. In such cases the reaction of Tortelli and Jaffe may be advantageously used. Further information is given by the specific gravity which lies between 0.9494 and 0.9384 for fish oil fatty acids and between 0.9314 and 0.9373 for fish oils themselves. It should be noticed that other hardened oils, in particular hardened linseed oil, give the above reaction. Hardened fish oils are identified with most certainty according to Marcusson and Meyerheim by means of their characteristic component, octadecylalcohol.

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Disinfection with Formaldehyde—Bleaching Powder as a Substitute for Permanganate. D. W. HORN, Ph. D. *Amer. Jour. of Public Health*, Feb., 1918. The permanganate method of disinfection is widely used in this country. In the tanning industry it has found application in connection with the foot and mouth disease. The amount usually recommended to disinfect 1,000 cubic feet of space is 75. cc. of formaldehyde gas.

This would require 500 cc. of formalin poured into 250 grams of potassium permanganate. On account of the high cost of permanganate the author has substituted bleaching powder.

He finds that 800 cc. of formalin poured into 620 grams of bleaching powder will produce the desired quantity of gas to disinfect 1,000 cubic feet (*i. e.*, 75 cc. formaldehyde).

He compares the cost of this method with the permanganate method, as well as the dichromate method recommended by the Pennsylvania Department of Health.

To produce 75 cc. of formaldehyde costs:

Permanganate—formalin method	$2.29
Dichromate—formalin method	1.14
Bleaching powder—formalin method	.39

Disinfection with Formaldehyde. C. G. STORM. *J. I. E. C.*, Feb., 1918. The author finds that soluble chlorates are a good substitute for permanganate. He has tried both potassium and sodium chlorates with formalin and finds both to give good results.

The best proportion to use is 25 grams of chlorate to 100 grams of formalin. This, however, requires heating to 65° C. to start the reaction. This is easiest done by putting the formalin and chlorate in a pail properly weighted and then placing this in a dishpan containing boiling water.

According to the author's figures it would require about 300 cc. of formalin and 75 grams of sodium chlorate to disinfect 1,000 cubic feet of space.

The Reclamation of Grease and Oil. KEITH MERRILL, in *Commerce Reports.*

(ABSTRACTOR'S NOTE.—The following article should be of interest to tanners, as somewhat similar methods have been used in the recovery of grease from scrap leather, floor scraping, etc.)

The grease removed in the cleaning of wheels, axles, and other parts of motor omnibuses, trucks, and other motor vehicles, is now utilized by the London General Omnibus Co. The process of reclaiming the oil is described in the *Commercial Motor*, December 27, 1917.

Before the war kerosene was largely employed for the cleansing of engines and other parts of vehicles, but now its consumption is restricted to the barest minimum, the net effect being the saving of five-sixths of the former consumption. Kerosene, as a matter of fact, is now only employed on certain parts of the mechanism for the cleaning of which

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there is no practical substitute. For the cleaning of wheels, axle casings, and front axles, a weak solution of hot caustic soda is employed.

When engines, gear boxes, back axles, or any other parts are stripped for overhaul, a very great saving is effected over former practice.

The unit is dismantled and the parts are placed in a cradle and dumped into a tank of water into which a jet of steam is turned so as to bring the water to boiling point. Caustic soda is added to the water until a solution of about 3 per cent. strength is obtained. The whole of the grease is removed from the parts in the process of boiling and comes to the top of the water. Before the contents are removed the grease is drawn off the top. This is done through an overflow pipe of large diameter which leads into a barrel.

The cradle of parts is then transferred to a second tank of clean, boiling water, which finishes the cleansing and, as the parts are drawn out quite hot, they drain perfectly dry and absolutely clean.

The result, so far as cleanliness of parts is concerned, is considerably better than if kerosene had been used. All minute parts of metal, dirt, and grit go to the bottom of the first cleansing tank, where there is a large drain cock, the tank occasionally being washed out and all the sediment drawn away.

The London General Omnibus Co. has a central depot for reclaiming oil and washing rags, and to this depot the barrels of waste oil, as they are obtained from the various garages, and the rags, are sent.

At this depot there is a battery of three tanks erected over a furnace, each of which is filled to about two-thirds with water, which is brought up to the boiling point. The barrels of oil as they come in are drawn off into the first boiling tank, a little being added at a time. The oil is thoroughly boiled, and when it overflows into the second tank (by the adding of more oil to the first) it has become almost fit for use again, but it passes into the second tank and is given a second boiling, and then on to the third tank where it goes through its final stage of cleansing, and from the last tank it is drawn off and run into barrels.

As to rags, their price to-day is much higher than before the war, when they were thrown away after being used. At present every rag is collected in each garage and sent once a week to the central cleaning depot. The first process through which they go is the extraction of all grease and oil in a centrifugal steam-heated chest like those in the ordinary dry-cleaning establishments in the United States. All oil, by the rotary action of this chest, is expressed from the rags, whence it runs into barrels for the reclaiming process already described. The rags are then put into a washing machine, and later into a rotary drying machine.

The oil gained by the reclaiming process is not entirely suitable for use again as a lubricator, but as so much of it comes from a solid grease, it is of a better quality than cleansed engine oil. It still has a value as a fuel, however, as can be gathered from the fact that at the North Road coach factory of the London General Omnibus Co., two 80 horse-power Diesel engines are run from the output of the oil reclaiming depot, leav-

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ing a certain quantity in excess available for sale. This oil is particularly good for Diesel engine work. It leaves the cylinder heads and valves very clean and is entirely satisfactory.

The cleansing plant of the London General Omnibus Co. has paid for itself in a very short time, because oil reclaimed may easily be sold for blending or fuel. A small plant can be easily put up in any garage, fuel for the furnace being rubbish and shop sweepings, or if the "raw material" is too small in quantity for economical handling on the spot, it could be collected and dealt with in larger bulk at some central collecting place.

Whale Fat for Margarin in Norway. *Commerce Reports.* On account of the shortage of other materials for the margarin industry, experiments have been made for some time with hardened whale fat. In Denmark whale fat has been in use ever since 1914, but in Norway it has not been necessary until recently to use this substitute for other fat. However, since the supply of the usual raw materials for this industry to Norway has now entirely ceased, the hardened whale fat will be used also by the margarin factories here, and to this effect the whale catching off the coasts of Norway is to be commenced for Government account. Whaling off the coast of Norway has been prohibited for a number of years, because the fishermen claimed that it scared the fish away from the coasts and that, moreover, the offal from the whaling stations is detrimental to the fish.

In 1914 Denmark used 20,000 barrels of hardened whale fat in the margarin industry. This product has been proved to be well suited for making a margarin that keeps well and tastes well and to be even better suited for making lard. For the latter purpose it is only necessary to add a smaller part of vegetable oil, such as cottonseed oil or soya oil, to make the lard thus produced fully as good as the imported American lard. In Denmark, where this fat has been used for nearly three years, no injurious effects on the human organism have been observed.

Hide Market at Shanghai. *Commerce Reports.* The greater proportion of the hides that reach this market are of the hard, sun-dried kinds, which come principally from Yangtze Valley points. Some dry-salted, and a very few wet-salted hides come to Shanghai. Anthrax is rare in China. A dealer here states that during thirty-five years' experience in the hide business he has personally known of only one case of anthrax. Danger from anthrax would be much greater among the wet-salted hides, but there is very little trade in this class of hides in Shanghai. If there were any danger it would certainly appear before the hides left the packers here.

Upon their arrival here the hides are carefully inspected and graded under the supervision of expert foreigners, and the best selected, in two grades, are sent to the United States. No poor grades are sent to that country. There is a brisk demand from Italy for the poorer grades of

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hides. After selection for shipment, the hides are all carefully cleaned by scraping and brushing. They are then disinfected by immersion in an arsenic bath and are carefully and thoroughly sun-dried again before they are packed in bundles for shipping.

The dry-salted hides come chiefly from the northern parts of Shantung and Chihli Provinces, and the only trouble with these is likely to come from inexperienced handlers in outside cities. No tare allowances are made by exporters except for the weight of the hoops around the bundles and the burlap that protects the corners. The hides are well flayed, resulting in the removal of every particle of meat. There is no tick except in Manchuria, and few hides come to this port from there. The tails and hoofs, and part of the face—the nose and eyes—are taken out. The hides are weighed separately to get the weights suitable for various markets and manufactures. The principal selling centers are Hankow, Shanghai, and Tientsin.

Wattle Bark in South Africa. C. DU PLESSIS CHIAPPINI. *J. R. S. A.*, Feb. 15, 1918. The production of wattle bark is one of the chief agricultural industries in the Natal Province. This bark, which is a splendid tanning agent, and is stripped from the black wattle tree (*Acacia mollissima*) indigenous to Southeastern Australia, was introduced into Natal about thirty years ago, and since its introduction an industry of first importance has been established.

The cultivation of wattle trees has proved very remunerative to the Natal farmer. The trees are ready for felling and the bark is stripped off when they are about six years of age. The grower usually cuts his trees in rotation, taking six or seven years to go through his plantation, when he commences again *ab initio*. The trees are self-sown, and, with a little care, again come to maturity in the usual time.

At present there are about 160,000 acres of land devoted to wattle growing, and the annual yield is approximately 65,000 tons of bark, which output is expected to increase considerably. The average price realized for dried bark, bagged and chopped, is from £5 to £6 per ton at Durban. The export of bark in 1907 amounted to 54,500,000 pounds, valued at £139,400, and during 1917, 93,532,000 pounds, valued at £225,722.

Wattle bark contains from 28 to 30 per cent. of tannin acid. One of the most valuable by-products is the timber, which is in great demand at the mines for pit props, the sale of which, in some instances, more than recompenses the growers for the cost of producing the bark.

Prior to the war very little wattle bark was used by the English tanners, and practically the only market was in Hamburg; but since the outbreak of hostilities the bark has been used in England with considerable success.

Shortly after the war broke out, some enterprising persons established factories in Natal for the manufacture of wattle extract; two factories

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are now producing the extract, and the new industry has proved to be very remunerative. The extract is of high tanning value and realizes good prices on these markets.

It is anticipated that the bulk of the bark produced in Natal will, after the war, be consumed by the local extract factories, and that more of these will be erected.

Recovery of Potash from Wool Scouring Waste. R. S. WESTON. *J. S. C. I.*, January, 1918. Wool scouring waste is one of the most befouling and greasy liquids which streams receive. It fouls the banks and bottoms, clogs sewers and outlets and increases the growth of aquatic vegetation. Its purification while important before the war, is doubly so now on account of the increased prices of the grease and potash which can be recovered from the waste.

Before the war the usual treatment was to precipitate with sulphuric acid and sodium sulphate. In this method the potash was lost. Since the war niter cake has been used in the place of sulphuric acid, but this also prevents recovery of the potash. The three main processes embodying the recovery of the potash which can be used are:

1. *Precipitation Process.*—The dirt is removed by settling, the grease by centrifuging, some other impurities are precipitated out by chemicals, and the potash recovered from the remaining liquor by evaporation, calcination and lixiviation.

2. *Cardem Process.*—This is a process used to reduce sulphate pulp liquor and tanning extracts to a powder.

The apparatus consists of a series of chambers through which hot flue gases are passed and into which the settled and centrifuged waste is sprayed through special nozzles. The potash is then recovered from the dried product.

3. The settled and degreased liquors are concentrated in an evaporator to 65 per cent. solids and the concentrated liquor coked in an open furnace, the potash being removed from the coke by lixiviation.

Various improvements have been made in the wool scouring mills which have improved their effluent, but still a recovery plant is not only necessary but profitable. The value of the products obtained, even at prices before the war, will more than pay for the process.

The Melting Point of Coal Ash. J. T. DUNN. *J. S. C. I.*, Jan., 1918. The author made a series of tests on the melting points of coal ashes. On account of the variation of the melting points, analyses were made of the ashes. These analyses together with their melting points are given in a table. The melting points run from 1,020° to 1,500° C. These determinations were made for a briquetting plant for iron ore, where the briquettes are taken in wagons through the furnaces. In the course of

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this operation considerable trouble resulted when a change of coal was necessary because of the failure of the usual supply, from the ash of the coal with which the furnaces were being fired being deposited in the wagons until they clogged up and jammed the furnaces. In the discussion which followed this paper, considerable stress was laid on the importance of the melting point in determining the value of coal.

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15TH ANNUAL MEETING, HOTEL TRAYMORE,

VOL. XIII. MAY, 1918 NO. 5

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CHANGES OF ADDRESS.

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FIFTEENTH ANNUAL MEETING.

The following program, subject to slight rearrangement, has been prepared for the Fifteenth Annual Meeting, at Atlantic City, N. J., May 16, 17, 18:

PROGRAM.

Morning Sessions Convening at 10 o'clock.
Afternoon Sessions Convening at 2 o'clock.

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THURSDAY MORNING, MAY 16, 1918.

Opening remarks by the President.....Chas. R. Oberfell
Report of the Secretary-Treasurer.....H. C. Reed
Committee Report .....J. S. Rogers
(Determination of Free Sulphuric Acid in Leather)
Committee Report.....H. R. Davies
(Testing of Coal-tar Dyes for Leather)
Committee Report.....C. R. Delaney
(Testing of Dyewood Extracts)

THURSDAY AFTERNOON, MAY 16, 1918.

12.00 Noon--Luncheon with the National Association of Tanners.
Toast to the President of the United States.....C. F. C. Stout
Address—Prof. Lincoln Hutchinson, Assistant Director of the Importers Bureau of War Trade Board
Address—(Speaker to be announced later)

FRIDAY MORNING, MAY 17, 1918.

All Day Joint Sessions with National Association of Tanners. (General Discussion on all subjects by Tanners and Chemists)
Problems for the Consideration of the American Leather Research Laboratory.....F. H. Small
Upper Leather for Army Shoes.....Fred A. Vogel

FRIDAY AFTERNOON, MAY 17, 1918.

Sole Leather for Army Shoes.....Dr. Allen Rogers
The Work of the Bureau of Standards in Leather.....P. L. Wormley
The Profitable Recovery of Proteids from Tannery Waste Water .....C. L. Peck

SATURDAY MORNING, MAY 18, 1918.

Committee Report.....T. A. Faust
(Effect of Hard Water on Tannins)
Committee Report.....Robt. W. Griffith
(Comparative Analysis)
Committee Report.....T. G. Greaves
(Small's Modification of the Hydrochloric Acid-Formaldehyde Method for Separating Tannins with Special Application to Chestnut Oak Bark and Chestnut Wood)

Executive Session.
Election of Officers.
Council Meeting.

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THEORY OF TANNING—A REPLY.

By John Arthur Wilson.

In the discussion of a subject so deeply involved as the theory of tanning, it is not surprising to find one mistaking lack of understanding for disagreement. Bennett, in his recent contribution to this subject, "The Lyotrope Series and the Theory of Tanning,"[1] states that he is in profound disagreement with the author's views on tanning, but the author feels impelled to express his belief that Bennett has not comprehended the theory of vegetable tannage evolved by Procter and Wilson[2] in consequence of which the equations given later by the author[3] might well appear to him unjustified.

On several occasions the author's attention has been drawn to persons unable to grasp the ideas contained in the recent publications of Procter and his collaborators because of an attempt to visualize conditions obtaining at equilibrium *without the aid of mathematics.* If the reader will refer to "The Acid-Gelatin Equilibrium"[4] he will find the equation

$$x^2 = y(y + z) \qquad (1)$$

expressing the ionic relation existing when gelatin is in equilibrium with dilute hydrochloric acid solution, where in the external solution x represents the concentration of hydrion or chloridion and in the solution absorbed by the gelatin y represents the concentration of hydrion and $y + z$ the concentration of chloridion. This relation is fairly readily visualized and indeed the principles underlying its derivation are to be found in numerous text books. But it has been stated that the total concentration of ions, $2\,y + z$, of the jelly *is greater than* the ionic concentration, $2\,x$, of the external solution. This fact is perhaps not so readily visualized, but is easily proved by applying to the above equation the well-known theorem of algebra: *If the product of unequals is equated to the product of equals, then the sum of those unequals is greater than the sum of the equals.* In other words, it was by an appli-

[1] *J. S. L. T. C.* 1, 130-136 and 169-182 (1917); This JOURNAL 13, 91 (1918).

[2] *J. Chem. Soc.* 109, 1327 (1916); This JOURNAL 12, 76 (1917).

[3] This JOURNAL 12, 108 (1917).

[4] *J. Chem. Soc.* 109, 307 (1916); This JOURNAL 11, 261 (1916).

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cation of mathematics that we learned that $y + (y + z)$ is greater than $x + x$ and obtained the equation

$$2x + e = 2y + z. \qquad (2)$$

Now the relations existing between the volume of the solution absorbed by the jelly, the amount of electrolyte combined with the gelatin, and the various ionic concentrations are so complicated that it is doubtful if any mind could picture them clearly without the use of mathematics. This will be illustrated to a striking degree later in this paper by an equation giving the volume of absorbed solution as a function of the hydrion concentration.

Returning now to Bennett's paper, we find him avoiding any quantitative treatment of the subject and attempting explanations without the aid of mathematics. He has incorporated into his paper a number of views expressed by W. W. Taylor,[5] especially those dealing with what is called *lyotrope influence*. Salt solutions are found to be less compressible than pure water, but equal concentrations of different salts of one anion or of one cation are found to produce effects of different degrees and we can arrange the ions in order of the effect produced; thus

$$CO_3 > SO_4 > Cl > Br > NO_3 > I \text{ and}$$
$$Na > K > Li > NH_4.$$

Because the effect is probably due to some action of the salt upon the solvent, Taylor refers to it as lyotrope influence. The same or a very similar order of ions is observed in their effects upon many other actions, such as the hydrolysis of esters, precipitation of sols, gelation, etc. Although this series is generally known by the name of its discoverer, Hofmeister, Taylor throughout his book calls it the lyotrope series. Now Bennett uses *lyotrope influence* as a sort of magic term which in itself is supposed to explain any action of any salt, whether it be on the compressibility of a solution or the contraction of a swollen jelly, two actions which the author is convinced are quite different. Bennett insists that this lyotrope influence is of primary importance to any satisfactory theory of tanning and yet he does not offer any explanation as to the molecular mechanism of this mysterious influence. One might equally well contend that no

[5] The Chemistry of Colloids (Longmans Green & Co.).

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satisfactory theory of tanning could be evolved which did not include a consideration of the relative migration velocities of the ions, temperature, or any secondary influences.

The lyotrope or Hofmeister series, however, is a fact and one is tempted to speculate as to why the order of ions should be practically the same for so many different actions. Taylor notes that certain salts lower the gelation temperature in the order

$$Cl < ClO_3 < NO_3 < Br < I$$

and that Pappada found neutral salts to accelerate gelation in the order

$$Cs > Rb > K > Na > Li.$$

To one who has followed recent work on the determination of the degrees of hydration of the ions, these series present a familiar appearance. In Table I are given some figures calculated by Smith[6] for the number of molecules of hydrated water held by these ions at zero concentration.

TABLE I.

Ion	Molecules of hydrated water	Ion	Molecules of hydrated water
Cs	3.7	Cl	9.6
Rb	6.4	ClO_3	9.3
K	9.6	NO_3	8.9
Na	16.9	Br	6.7
Li	24.0	I	4.3

There is here an evident coincidence between the so-called lyotrope series and the hydration series. More recently Kendall, Booge and Andrews[7] have concluded from their work that, for acids in aqueous solution, hydration increases with the acidic strength. For salts of these acids, however, the series appears to be reversed, the salts of the strongest acids, such as NaCl, being less hydrated than those of weak acids, such as CH_3COONa and Na_2CO_3. Taylor points out that the order of anions arranged according to their precipitating power on neutral albumin is completely reversed if a trace of acid be added to the albumin, furnishing another striking similarity between the hydration and lyotrope series.

Kendall, Booge and Andrews hold that for aqueous solutions of *acids* and *bases,* the extent of hydration increases with the acidic

[6] *J. Am. Chem. Soc.* **37**, 729 (1915).

[7] *J. Am. Chem. Soc.* **39**, 2303 (1917).

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or basic strength; in other words *the greater the degree of hydration the greater the degree of ionization.* If this could be extended to all electrolytes we should find equimolar concentrations of different salts furnishing different ionic concentrations following the lyotrope order and this in itself would be sufficient to account for the series. But unfortunately for this view, uni-univalent salts appear to be about equally dissociated while hydration values are apparently widely divergent. One awaits with interest the promised publications by Kendall and his collaborators on the question of salt hydrates. Meanwhile the fact remains that as yet no entirely satisfactory explanation of the molecular mechanism responsible for the lyotrope series has been forthcoming and we should hardly be justified in trying to explain the action of tanning by means of this series, the mechanism of which is itself not understood.

Turning now to the subject of *adsorption,* the author objects to Bennett's free use of the term without his offering an explanation as to what is that mechanism of adsorption upon which one can build a satisfactory theory of tanning. The author questions Bennett's authority for the statements: "Moreover, the adsorption law is not merely empirical; whatever its origin, it now rests upon as sound a basis of theory as the ionization theory. The adsorption law is almost a necessary deduction from surface tension phenomena and rests upon equally well founded assumptions." Ever since Gibbs showed that, where a solute lowers the surface tension of a solution, the concentration of the solute must be greater at the surface than in the bulk of solution, there has been a strong tendency to use this proof as an explanation of the fact that substances of great specific surface reduce the concentration of solute in many different kinds of solutions with which they are brought into contact. It cannot be emphasized too strongly that Gibb's work applies only to true solutions. Since it has generally been found impossible to determine the actual concentration of solute in the layer of solution in direct contact with the surface of the adsorbing agent, any conclusions as to the causes of such adsorption have been open to question. Differences of opinion have arisen because of our imperfect understanding of the nature of the forces involved in surface tension, which may not be different from those resulting in solvation or in the union

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of NH_3 and HCl. It is quite possible, if not probable, that many cases of adsorption are actually chemical combinations of portions of the solute with the surface molecules of the adsorbing agent. In accounting for the electrical charge possessed by colloidal particles Burton[8] says: "There can be no doubt that this charge is due primarily to some chemical combination followed by a partial dissociation of a portion of the colloidal unit." He refers further to a paper[9] in which he "has given evidence to show that the charge possessed by the metallic particles of the Bredig electrically prepared solutions is due to a chemical reaction between the medium and the metal followed by dissociation." Zsigmondy[10] "has come to the conclusion that the adsorption and dissociation of ions by the particles offers the only rational explanation of the coagulation and peptisation by electrolytes." Ostwald[11] says: "If it is asked what forces bring about these concentration changes in surfaces, it can only be answered that *a whole series of different kinds of energy* plays a role." The subject is indeed involved and agreement upon it is not yet complete. With such a state of affairs, it is easy to devise numerous theories which will fit the facts qualitatively. Consequently such theories are of little weight compared to one which explains the facts quantitatively. Bennett makes no attempt at a quantitative treatment of the subject.

Because of the enormous complexity of the problem, it has seemed to the author that deductive reasoning from a simple hypothesis offers the only hope of a satisfactory solution. Such an hypothesis has been furnished by Procter in his quantitative treatment of the acid-gelatin equilibrium, from which he concluded that gelatin forms a highly ionizable chloride with HCl. Procter is not alone in holding this view; for example on page 219 of Zsigmondy's book (*loc. cit.*) we find the following equations given for the action of acids and alkalis on proteins.

[8] The Physical Properties of Colloidal Solutions (Longmans Green & Co.) p. 181.

[9] *Phil. Mag.* 11, 425 (1906).

[10] Chemistry of Colloids (John Wiley & Sons, 1917) p. 73.

[11] Theoretical and Applied Colloid Chemistry (John Wiley & Sons, 1917) p. 121.

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$$R\begin{cases}NH_2\\COOH\end{cases} + HCl \rightleftharpoons R\begin{cases}NH_3^+\\COOH\end{cases} + Cl'$$

$$R\begin{cases}NH_2\\COOH\end{cases} + NaOH \rightleftharpoons R\begin{cases}NH_2\\COO'\end{cases} + Na^+ + H_2O.$$

(These are not very different from the equations which Bennett termed "blood curdling.")

In a paper soon to appear[12] W. H. Wilson and the author have reasoned out, *without regard to experiment,* what should result when an elastic jelly is immersed in a solution of a uni-univalent electrolyte with which it combines chemically after the manner of protein and HCl in the above equation. The equations which have been derived are very general and apply to suspensoids as well as emulsoids, but special emphasis will be laid here upon their application to the hydrochloric acid-gelatin equilibrium, the reader being referred to the paper mentioned for a more general treatment. Complete ionization of the gelatin chloride and hydrochloric acid is assumed, for otherwise the relations become exceedingly complicated. However, since only concentrations less than N/5 will be considered, very little error will result from this assumption.

It is clear that equations (1) and (2) apply and therefore need not be rederived. V is defined as the number of cubic centimeters of solution absorbed by, and therefore also the increase in volume of one millimole of gelatin. All concentrations are in terms of moles per liter. Two constants are involved, defined as follows:

$$C = \frac{e}{V} \qquad (3)$$

which gives a measure of the modulus of elasticity of the gelatin.

$$K = \frac{[\text{unhydrolyzed gelatin}] \times [H^+]}{[\text{gelatin ion}]} \qquad (4)$$

which corresponds to the constant governing the dissociation of ammonium ion into ammonia and hydrion.[13]

[12] Colloidal Phenomena and the Adsorption Formula. *J. Am. Chem. Soc.*, (June, 1918).

[13] NOTE: A better understanding of this work will result from reference to "The Swelling of Colloid Jellies;" This JOURNAL 11, 399 (1916), or to "The Acid-Gelatin Equilibrium" (*loc. cit.*).

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Since we are dealing with one millimole of gelatin,

$$[\text{unhydrolyzed gelatin}] = \frac{1}{V} - z$$

where z is the concentration of gelatin ion, and since the concentration of hydrion in the jelly is represented by y, we have

$$K = \frac{\left(\frac{1}{V} - z\right) y}{z}$$

or $$Vz\,(K + y) = y \qquad (5)$$

From (1), (2) and (3) $$z = CV + 2\sqrt{CVy} \qquad (6)$$

And substituting (6) in (5)

$$V\,(K + y)(CV + 2\sqrt{CVy}) = y \qquad (7)$$

Likewise from (1), (2) and (3)

$$x = y + \sqrt{CVy}. \qquad (8)$$

Equations (7) and (8) can readily be solved simultaneously, giving V as a function of x, but the resulting equation is so unwieldy that it is preferable to keep them separate. By running successive portions of standard HCl into a gelatin solution of known volume and determining the hydrion concentration by means of the hydrogen electrode, after each addition, Procter and Wilson obtained the value K = 0.00015. The constant C was determined from e and V and was found to decrease with rise of temperature being about 0.0003 at 18°C. Substituting these values in the equations we get the curves shown in Fig. 1 and 2. In these figures are also indicated actual determinations made by Procter[14] before these constants were known.

It is important to note that the comparison of theoretical and experimental values in Fig. 1 does not require a knowledge of the molecular weight of gelatin. The experimental values for concentration of gelatin chloride are taken as the difference between the concentrations of chloridion and hydrion in the jelly.

As for the comparison of results in Fig. 2, it is necessary to know the molecular weight of gelatin. Since the author has found that if gelatin be considered as a monacid base its molecular weight would be 768, Procter's values for V have been altered so

[14] *J. Chem. Soc.* **105**, 317 (1914); This JOURNAL **9**, 212 (1914).

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as to indicate the amount of solution absorbed by 0.768 gram gelatin.

The two figures really constitute separate proofs, Fig. 1 that the hypothesis is correct and the constants reasonably accurate,

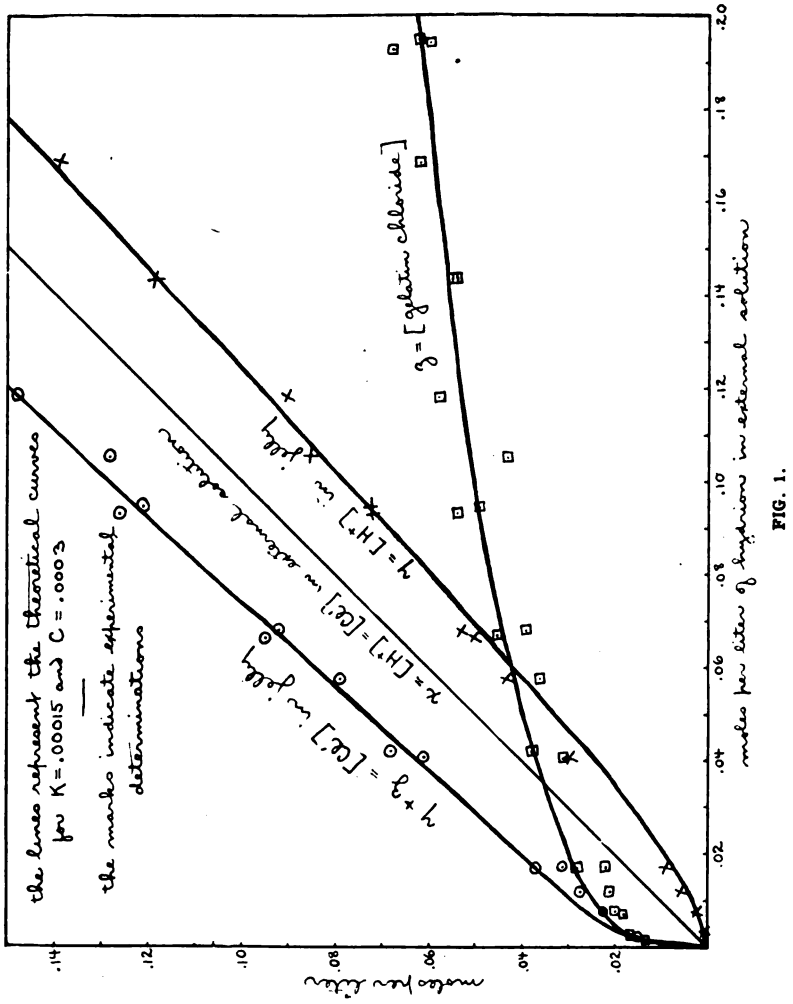

FIG. 1.

and Fig. 2 that the molecular or equivalent weight of gelatin is at least of the order of magnitude of 768. Such agreement between pure reasoning and experimental facts can hardly be called accidental and whoever has an alternative theory to propose, or de-

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fend, should first examine it to determine whether or not it will explain the facts quantitatively as does this one.

The author regards the foregoing as the strongest kind of evidence that with gelatin and acids we are dealing with ionic re-

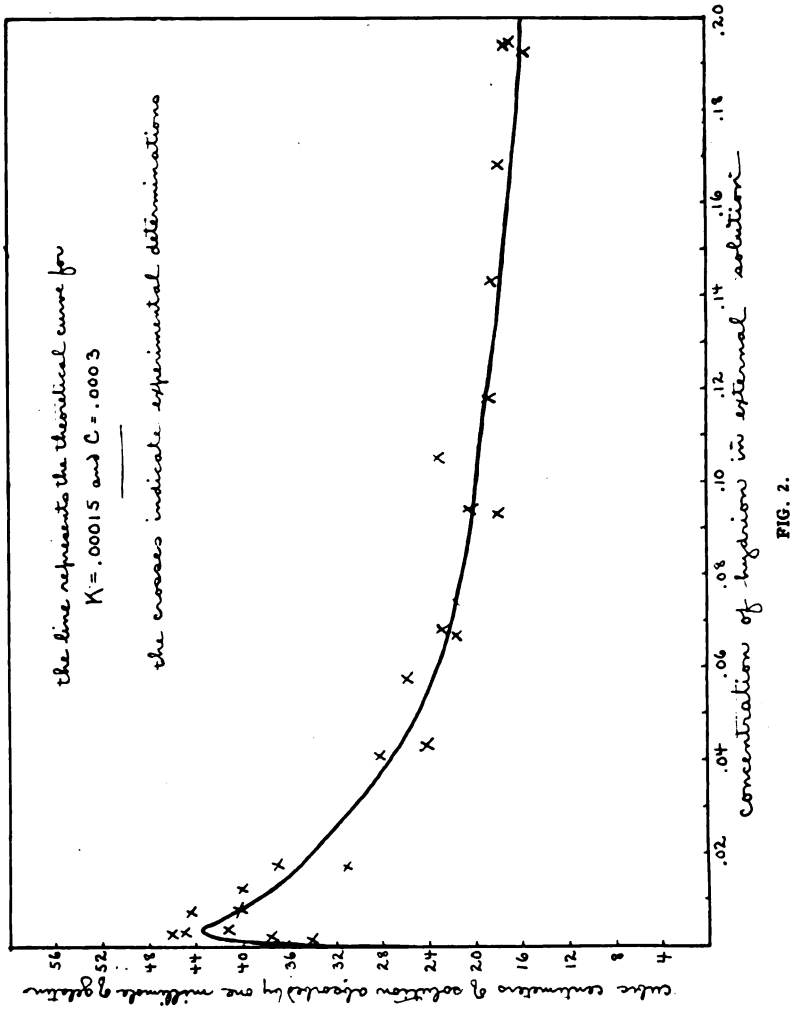

FIG. 2.

actions and that in acid solution the positive electrical charge on gelatin or hide is due to the ionization of a gelatin or collagen salt of that acid. This conception is the basis of the theory of vegetable tanning of Procter and Wilson and furnishes the

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author's reason for believing vegetable tanning to be an ionic reaction. If Bennett agrees with Burton's view (*loc. cit.*) concerning the origin of the electrical charge on colloids, the author would like to have him explain his distinction between chemical and electrical equivalence.

As for chrome tanning, the author has been entirely unable to grasp the procedure by which Bennett changes the sign of the electrical charge on colloidal chromic oxide, making it capable of precipitation by positively charged collagen. Furthermore, it has yet to be proved that the chrome in a one-bath liquor is in the colloidal state. In a private communication Dr. A. W. Thomas of Columbia University informed the author that a determination of $[H^+] = 0.00076$ had been obtained by means of the hydrogen electrode for a commercial chrome liquor rendered basic until the chrome had begun to precipitate. It was found that such a liquor would tan slightly acid pelt without any further addition of alkali. Even in neutral chromic oxide sols the particles are positively charged, while in this solution the hydrion concentration is 7600 times as great as that of a neutral solution. Because colloidal chromic oxide as well as collagen is positively charged in acid solution and since chrome tanning takes place entirely in acid solution, the author was forced to abandon the idea of mineral tanning being a colloidal coprecipitation. The idea that it is merely a coating of the fibers with chromic oxide will not suffice in view of the resistance of chrome leather to boiling water. Collagen is converted into gelatin by immersion in water at the boiling point, but chrome leather is practically unaltered by this treatment, an indication that what was collagen in the leather has undergone chemical change. The only rational possibility left, in the author's opinion, is that the chrome combines with the collagen forming an actual compound, possibly analogous to chromic acetate. The author has from time to time carried out experimental work on this subject and intends to continue the work as opportunity is afforded.

And now for a final word on the subject of the Freundlich adsorption formula. This equation apparently does represent the facts approximately. Bancroft[15] says, "no formula is strictly accurate, and the simplest one seems best for the time being. If

[15] *J. Franklin Inst.*, **185**, 203 (1918); Abstract this JOURNAL, this issue.

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the curves really bend round parallel to the axis of ordinates, the simple formula is necessarily wrong."

Our curve for gelatin chloride in Fig. 1 can be represented very closely by

$$z = 0.1\, x^{0.3}.$$

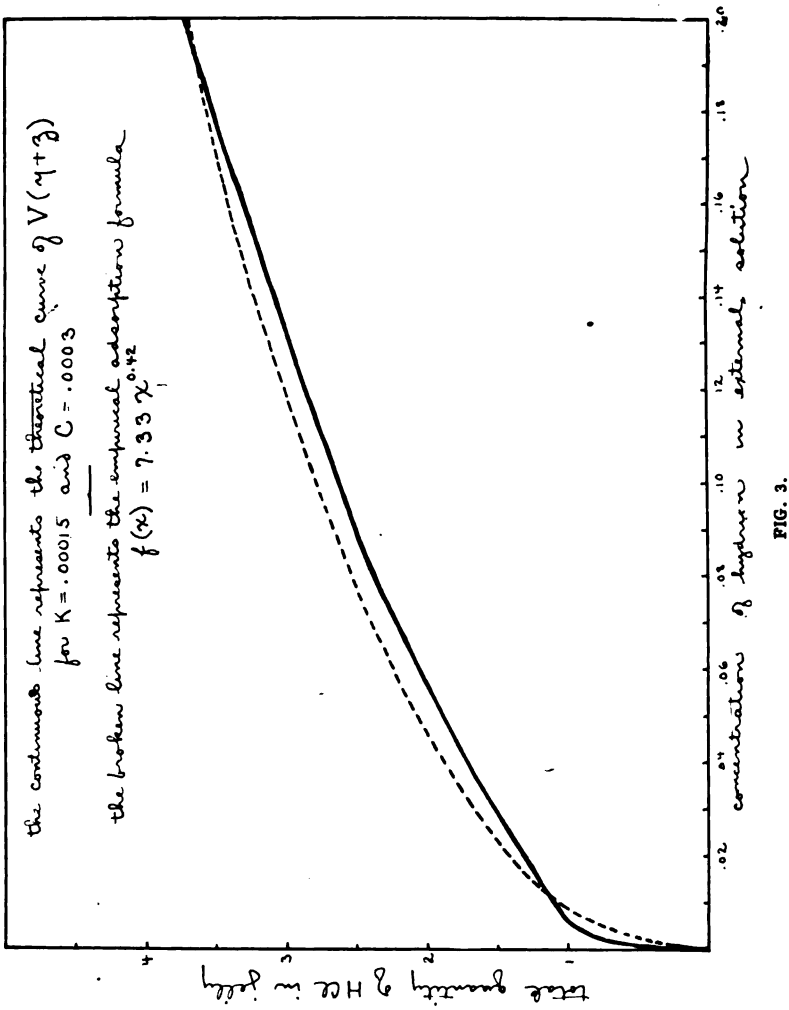

FIG. 3.

Since it agrees with the empirical formula, are we to call the combination of gelatin and HCl adsorption? If so, then such

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adsorption is really chemical combination. Mr. Wm. Harrison calls attention to the fact that it is not z, but $V(y+z)$ which is determined in certain adsorption experiments. The curve for $V(y+z)$ as a function of x is given in Fig. 3 along with the curve for $7.33\ x^{0.42}$ which would be that of the empirical formula. The difference between these curves is of about the same order as is generally found between observed results and those calculated from the empirical formula. By a suitable juggling of constants in this formula, which is quite permissible, the two curves can be made to approximate each other over wide ranges.

The author's real objection to the empirical formula is not that it does not *represent* the facts approximately, but rather that it does not *explain* the facts as a true formula should do. There is reason to believe that adsorption is due primarily to chemical combination, whether by means of primary or residual valencies, between the adsorbing agent and substance adsorbed and that further development of the mathematical relations given above will ultimately result in a formula which will give a true and exact explanation of the adsorption of dissolved substances by colloids.

The more specific details of Bennett's papers are left untouched because they are for the most part corollaries of the main points and it is considered unwise to run the risk of befogging fundamental issues by a mass of detail.

Summary.

It is contended that Bennett's disagreement with the author's views on tanning is due to a lack of understanding of the recent work of Procter and Wilson. Such failure to comprehend this work has been common and is attributed to an attempt to avoid the mathematical treatment of the work.

An apparent relation between hydration and so-called *lyotrope influence* is indicated, but objection is raised to using this term as an explanation of the molecular mechanism of any action until the mechanism of this *influence* is itself understood.

The origin of the electrical charge on colloids is discussed.

By pure reasoning from the hypothesis that gelatin combines chemically with HCl forming a highly ionizable salt, an equation is derived which is in rigid quantitative agreement with experi-

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mental observations. Since many theories will explain the facts qualitatively, it is argued that any alternative theory proposed should be in as close quantitative agreement with the facts. This is Bennett's weak point.

Strong evidence is given that the electrical charge on gelatin or hide in acid solution is due to the ionization of a protein salt of that acid, which conception is the basis of the theory of vegetable tannage of Procter and Wilson.

The theory of chrome tanning is discussed and the opinion given that the formation of a chromium salt of collagen offers the only rational explanation as yet given.

A discussion is given concerning the Freundlich adsorption formula.

ANALYSIS OF SULPHONATED OILS.

COMMITTEE REPORT, 1917-1918.

By W. K. Alsop.

The Council requested me to act as chairman of this committee in order to make such recommendations in reference to changing our provisional methods as seemed advisable in view of last year's committee report. This was to be done without undertaking any further analytical work this year.

An article on Sulphonated Oil Analysis by Ralph Hart was published in the *Journal of Industrial and Engineering Chemistry*, Sept., 1917, and reprinted in this JOURNAL October, 1917, p. 550. This paper described some methods which it seemed might be applicable to the class of oils used in the tanning trade and I have decided to recommend that they be investigated by a committee and in the meantime that it is not advisable to make recommendations in reference to changing the present methods. Some tests with the methods proposed by Mr. Hart have been made in the laboratory of the Elk Tanning Co. and the paper by Mr. Schultz in this number gives results as compared with the present methods and may be of assistance to the committee appointed to take up the matter.

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ANALYSIS OF SULPHONATED OILS.

By G. W. Schultz.

The method of R. Hart (*J. Ind. and Eng. Chem.*, Sept., 1917; this JOURNAL, Oct., 1917, p. 550) was used with several additions and modifications to make it applicable to the analysis of all sulphonated oils and to include several other determinations.

Hart's use of the acid value of the fatty acids from the original oil for calculating the total fat should make his results too low, as it is well known that the saponification value of the fatty acids from a sulphonated oil is much lower than the acid value of the fatty acids from the same oil before sulphonation. This difference varies for different oils and with the degree of sulphonation. Even in the case of castor oil the average likely would be nearer 180 than 190.

The additions and modifications used are as follows:

Unsaponifiable.—About 20 grams of the sulphonated oil is accurately weighed into an erlenmeyer flask and saponified with 75 cc. of standardized alcoholic KOH approximately by boiling for 1 hour under reflux. Titrate the excess of KOH with N/2 acid using phenolphthalein and calculate to milligrams KOH/gram = *saponification value of sample.* Make the solution strongly alkaline again and add sufficient water to give a 50 per cent. alcoholic solution and boil for a few minutes under reflux, cool, transfer to a separatory funnel washing flask with successive portions of 50 per cent. alcohol and finally with petroleum ether. Extract soap solution at least three times with petroleum ether. The petroleum ether extract is then washed thoroughly, poured into a tared beaker, evaporated, cooled and weighed.

Saponification Value of Fatty Acids.—The extracted soap solution from above determination is boiled to dryness in an evaporating dish, stirring constantly to prevent scorching. The soap is dissolved in boiling water and boiled to expel alcohol. The fatty acids are precipitated with dilute acid and boiled until the liquids are clear. Transfer to separatory funnel and extract with ether. Wash the ether extract with concentrated Na_2SO_4 solution until free from mineral acidity. Distill off ether, evaporate to dryness

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by using small quantities of alcohol—filter through hot water filter and collect about 3 grams in a tared erlenmeyer. Weigh accurately and determine the saponification value in the usual manner. The saponification value is determined because there will be lactones or anhydrides present that have been formed by hydrolysis and the acid value would not give the desired result. Several examples are given below to show the difference between the saponification value and acid value of these fatty acids.

Combined and Free Fatty Acids.—If NH_3 be present in the oil it is necessary to determine the acidity in this manner—about 10 grams of the oil accurately weighed are dissolved in 50 cc. of 95 per cent. alcohol and titrated with N/2 NaOH to end point with phenolphthalein. The mixture is then boiled until free from NH_3 (about ½ hour) cool—add N/2 NaOH again to end point and boil again until no more NH_3 is evolved, cool, add sufficient N/2 NaOH to give the end point indication. Dilute largely with water and titrate with N/2 H_2SO_4 to acid end point with methyl orange. From the number of cubic centimeters of N/2 H_2SO_4 used (to neutralize the alkali combined as soap) is calculated the number of milligrams KOH per gram of oil necessary to neutralize the free fatty acids and those combined (originally) as soap.

If no NH_3 be present it is only necessary to determine the acid value of the sample in the usual way and add to this the number of milligrams KOH/gram corresponding to the total alkali combined as soap.

This value is used to calculate the per cent. of neutral fat in the sample as follows:—Take the saponification value of the sample, minus the negative alkalinity, due to NH_3, expressed in milligrams KOH/gram; from this subtract the combined and free fatty acids, expressed in milligrams KOH/gram; divide this result by the saponification value of the fatty acids, and multiply this result by 100. The product is the per cent. of neutral fat.

Below are given the results of the analysis of four different samples of sulphonated oils using this method compared with the method used by the A. L. C. A. Committee last year. The former method is designated as "new" the latter as "old." All determinations of the new method were run in duplicate and were check determinations while those of the old method were not.

The results for neutral fat are higher in every case by the new

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method and in spite of the great difference between the results of the two methods I am inclined to accept those of the new method as correct. These results for neutral fat can be checked very satisfactorily which is more than I can say for the "old" method.

	A		B		C		D	
	Old	New	Old	New	Old	New	Old	New
Moisture	14.34		21.29		34.65		32.34	
Ash	2.84		4.03		0.05		4.56	
NH_3	0.30	0.23	0.24	0.25	1.37	1.23	none	none
Unsaponifiable	25.98	26.20	0.72	0.68	0.24	0.24	14.49	14.50
Total SO_3	3.27		4.28		4.57		1.57	
SO_3 in salts	0.29		0.35		0.65		0.20	
Combined SO_3	2.98	2.75	3.93	3.74	3.92	3.63	1.37	1.15
Sulpho-fatty acids	14.15	13.07	18.67	17.77	18.62	17.24	6.50	5.46
Total fatty matter	52.27	54.57	71.06	69.84	57.56	56.88	47.87	45.00
Neutral fat	15.54	24.60	22.60	33.68	6.86	14.67	9.00	15.91
Sap. value of fatty acids	188.2		190.0		188.1		202.9	
Acid value of fatty acids	162.7		165.0		172.2			

These are cod oils or mixtures with this oil as the principle ingredient.

The determinations that are necessary by the new method are:

(1) Moisture and ash according to the old method.

(2) Total alkali—alkali combined as soap expressed in milligrams KOH/gram.

(3) Alkali with NH_3—expressed in milligrams KOH/gram.

(4) Unsaponifiable and *saponification value* expressed in milligrams KOH/gram.

(5) Saponification value of mixed fatty acids.

(6) Combined SO_3.

ELK TANNING CO. LABORATORY,
April, 1918.

THE ACIDITY OF CHROME LIQUORS.

Arthur W. Thomas, Ph. D., and Mabel E. Baldwin, M. A.

A series of careful measurements of the concentrations of hydrogen ion of chrome liquors and chromium sulphate solutions, by the electrometric method, shows that the "basicity" ratio is an inadequate and in fact misleading method of expressing the reaction of chrome liquors.

The increasing use of chrome tannage has made necessary more accurate chemical control and greater knowledge concerning the chemistry involved. Throughout the studies that have been made

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of the methods of analysis of chrome liquors there has frequently been felt a need of an accurate knowledge of the actual acidity of the liquors, that is, the exact concentration of hydrogen ion, as can be obtained only by the electrometric method. The methods now in use which consist of titrating with standard alkali in the presence of an indicator and which vary among themselves not in principle but in details of manipulation all measure the "total acidity." By "total acidity" is meant all the acid hydrogen both ionized and unionized while by "actual acidity" is meant only the ionized hydrogen. Since the hydrogen ion is the active principle of all acids and acidic properties are in direct proportion to the concentration of hydrogen ion we should expect that wherever the acidity of a chrome liquor has influence on its tanning power this influence would be mathematically related not to the total acid hydrogen but to the actual concentration of hydrogen ion. This idea that it is "actual acidity" and not "total acidity" which functions in the tanning process is not new. That it has been appreciated before is seen in the mention that is now and then made of the probability of a relationship between swelling effect and "actual acidity." It has not been so much a lack of realization of the difference between the total acid hydrogen and the exact concentration of hydrogen ion as a lack of equipment for measuring the difference that has hindered progress toward a better understanding of the relationship between the "actual acidity" and the tanning power of chrome liquors. Although Wood, Sand, and Law* have made careful measurements by the electrometric method their work has been on tan liquors and not on chrome liquors. They compared the results thus obtained with those obtained by titrating in the presence of indicators and even while believing that the actual concentration of hydrogen ion functioned in the tanning process, at the end of their paper they said, "It still remains to interpret the results in terms of direct value to the tanners."

Because of the demand for accurate measurements of the concentration of hydrogen ion in chrome liquors we present the data which follow, as the first of our series of researches on the chemistry of chrome tanning.

* Wood, Sand, and Law, *J. S. C. I.*, **30**, 3, 872 (1911); this JOURNAL, **6**, 114, 428 (1911).

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In the tables which follow are measurements of the exact concentrations of hydrogen ion in a chrome liquor under conditions which were these: First, solutions were made from a stock chrome liquor by adding water in increasing amounts so as to give a series of dilutions. Then at a given dilution a series of solutions were made containing definite amounts of acid and alkali. For each solution the value of the concentration of hydrogen ion in moles per liter was determined. These solutions were allowed to stand from 2 to 9 days and the concentrations of hydrogen ion again determined. Then after from 30 to 50 days the determinations were repeated. All these results are compared with the "basicity value," and prove the inadequacy of the latter.

The stock chrome liquor which was used in making these solutions gave by analysis 230.9 grams Cr_2O_3 per liter and 214.6 grams SO_3 per liter by the methods outlined in the Official Methods of the American Leather Chemists Association (1917). The "basicity" value is then 1.076 and the formula $Cr(OH)_{1.2}$-$(SO_4)_{0.88}$.

The experiments upon the stock chrome liquor were duplicated with pure chromium sulphate. A concentrated solution of pure chromium sulphate was made by dissolving the crystals in water and filtering. The most concentrated solution thus obtained contained less chromium than the chrome liquor but the dilutions were made so that corresponding solutions contained equal quantities of chromium.

Effect of Dilution.

The values of the logarithms of the concentrations of hydrogen ion in Table I and the curves B and C represent the change in the concentration of hydrogen ion of a stock chrome liquor upon dilution, while the change taking place in a chromium sulphate solution is shown in Table I and the curves E and F.

These dilution curves have for abscissas the number of times the original liquid was diluted and for ordinates the logarithms of the concentrations of hydrogen ion. The values termed the logarithms of the concentrations of hydrogen ion (Log. C_H+) are the negative exponents to which the number 10 must be raised in order to express the concentration of hydrogen ion in gram

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TABLE I.—EFFECT OF DILUTION.

Stock Chrome Liquor.

Solution No.	Dilution	Gm.Cr_2O_3 per liter	cc. N/2 acid per liter	Gm.SO_3 per liter	$\frac{Cr_2O_3}{SO_3}$ (1)	Log.C_H+ (2)* immediately	Log. C_H+ (3)* after 7 days
1	Stock Chrome Liquor	230.90	10720.0	214.60	1.076	2.31	2.31
	No.						
2	1 diluted 10 times	23.09	1072.0	21.46	1.076	2.96	3.17
3	1 diluted 20 times	11.55	536.0	10.73	1.076	3.09	3.26
4	1 diluted 40 times	5.77	268.0	5.36	1.076	3.27	3.31
5	1 diluted 80 times	2.89	134.0	2.68	1.076	3.30	3.32
6	1 diluted 800 times	0.29	13.4	0.27	1.076	3.60	3.61

Chromium Sulphate Sclution.

Solution No.	Dilution	Gm.Cr_2O_3 per liter	cc. N/2 acid per liter	Gm.SO_3 per liter	$\frac{Cr_2O_3}{SO_3}$ (4)	Log. C_H+ (5)* immediately	Log. C_H+ (6)* after 9 days
100	Concentrated $Cr_2(SO_4)3$ Solution	137.60	8908.8	178.35	0.770	1.60	1.60
	No.						
101	100 diluted 2.97 times	46.18	2993.4	59.92	0.770	2.13	2.13
102	100 diluted 5.94 times	23.09	1496.7	29.96	0.770	2.30	2.26
103	100 diluted 9.93 times	13.86	897.1	17.96	0.770	2.43	2.33
104	100 diluted 23.81 times	5.77	374.2	7.49	0.770	2.63	2.44
105	100 diluted 47.62 times	2.89	187.1	3.75	0.770	2.80	2.58
106	100 diluted 476.20 times	0.29	18.7	0.37	0.770	4.11	3.23

*For values of Log. C_H+ in concentration of hydrogen ion in moles per liter see Table II.

[1] Curve A, Fig. 1. [2] Curve B, Fig. 1. [3] Curve C, Fig. 1. [4] Curve D, Fig. 2. [5] Curve E, Fig. 2. [6] Curve F, Fig. 2.

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TABLE II.

Log. C_{H^+}	Conc. H^+ in moles per liter	Log. C_{H^+}	Conc. H^+ in moles per liter
1.60	0.02512	3.09	0.00081
2.13	0.00741	3.17	0.00068
2.26	0.00547	3.23	0.00059
2.30	0.00501	3.26	0.00055
2.31	0.00490	3.27	0.00054
2.33	0.00468	3.30	0.00050
2.43	0.00372	3.31	0.00049
2.44	0.00363	3.32	0.00048
2.58	0.00263	3.60	0.00025
2.63	0.00234	3.61	0.00024
2.80	0.00158	4.11	0.00008
2.96	0.00110		

molecules (moles) per liter. For example, the expression, Log. $C_{H^+} = 3.3$ is identical with the expression, concentration of hydrogen ion $= 10^{-3.3}$ moles per liter or 0.0005 moles per liter. As the value, Log. C_{H^+}, represents negative exponents the smaller the numerical value of Log. C_{H^+} the larger the concentration of hydrogen ion.

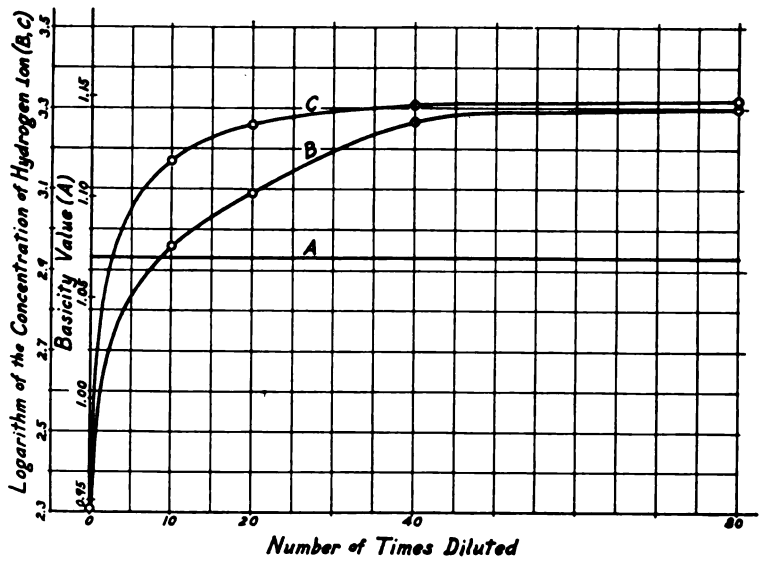

FIG. 1.—THE EFFECT OF DILUTION UPON THE ACIDITY OF A CHROME LIQUOR.

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In plotting curves of this kind it is convenient to use, not the absolute values of the concentrations of hydrogen ion, but their logarithms. In fact if the unit of ordinates were any absolute quantity of hydrogen ion it would hardly be possible to represent graphically the relation between dilution and concentration of hydrogen ion. If, for example, the quantity $10^{-3} = 0.001$ moles per liter is taken as the unit of ordinates, then a change in ionic concentration from 10^{-1} to 10^{-2} would on the axis of ordinates be equal to a change from 100 to 10 while a change from 10^{-4} to 10^{-5} would be equal to a change from 0.1 to 0.01. On the other

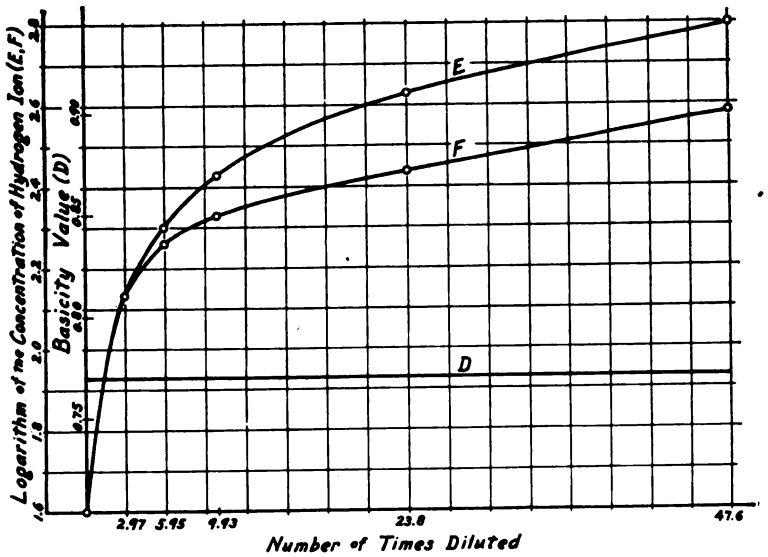

FIG. 2.—THE EFFECT OF DILUTION UPON THE ACIDITY OF A CHROMIUM SULPHATE SOLUTION.

hand, when the ionic concentrations are represented by their logarithms a change from 10^{-1} to 10^{-2} signifies a change equal to that from 10^{-4} to 10^{-5}. Although it is for convenience that the logarithmic values are used for ordinates it may be that the hydrogen ion enters, not with its absolute value, but with the logarithm of its value, into the equation which expresses the relation between the concentration of hydrogen ion and dilution.

From a study of these results it is evident that a change takes place in a chrome liquor when it is diluted which is in no way in-

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dicated by the "basicity" value. Moreover, this change is a change in the concentration of a constituent which, according to the consensus of opinion, is a very important factor in the tanning process, namely, the hydrogen ion.

In the original stock chrome liquor (dilution number 1) the concentration of hydrogen ion was 0.0049 moles per liter. When this liquor was diluted 20 times (dilution number 3) and a determination made immediately the concentration of hydrogen ion was 0.0008 moles per liter. After this solution (dilution number 3) had stood for 7 days and the concentration was again determined there were 0.00055 moles per liter. Readings taken after one week indicated practically no further change. The change in actual acidity taking place in a chrome liquor upon dilution is, therefore, not complete immediately after dilution but continues throughout several days, the chrome liquor becoming gradually less acid until finally ionic equilibrium is reached. Meanwhile a precipitate settles out. When the original liquor was diluted 800 times (dilution number 6) the concentration of hydrogen ion was 0.00025 moles per liter. In solutions as dilute as this equilibrium is reached almost immediately. For each one of these solutions the "basicity" value was found to be 1.076.

In the most concentrated chromium sulphate solution (dilution number 100) the concentration of hydrogen ion was 0.02512 moles per liter. When this solution was diluted 476 times, giving the same concentration of chromium as solution number 6, the concentration of hydrogen ion was, immediately upon dilution 0.00008 moles per liter, and after 9 days 0.00059 moles per liter. These figures show that, after a chromium sulphate solution has been diluted the acidity increases slowly until finally ionic equilibrium is reached. No precipitate settled out from the pure chromium sulphate solutions. For each one of these solutions the "basicity" value was 0.770.

By comparing these figures it is evident that there is a considerable difference in "actual" acidity between different dilutions of the same chrome liquor and the "basicity" value, being the same figure for each dilution, is inadequate for expressing this difference.

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TABLE III.—Effect of Added Acid and Alkali.

Stock Chrome Liquor.

Solution No.	Dilution and Amount of Alkali Added	Gm. Cr_2O_3 per liter	CC. N/2 acid per liter	Gm. SO_3 per liter	$\frac{Cr_2O_3}{SO_3}$ (1)	Log. C_H+ immediately (2)*	Log. C_H+ after 2 days (3)*	Log. C_H+ after 50 days (4)*
11	25 cc. 21 + 0.0 cc. N/5 NaOH + 25.0 cc. H_2O	13.86	643.45	12.88	1.076	3.19	3.31	3.33
32	" " " " " 2.5 " " " " 22.5 " "	13.86	623.45	12.48	1.110	3.35	3.35	3.35
33	" " " " " 5.0 " " " " 20.0 " "	13.86	603.45	12.08	1.147	3.51	3.39	3.37
34	" " " " " 10.0 " " " " 15.0 " "	13.86	563.45	11.28	1.228	3.68	3.47	3.44
35	" " " " " 12.5 " " " " 12.5 " "	13.86	543.45	10.88	1.274	3.97	3.54	3.46
36	" " " " " 15.0 " " " " 10.0 " "	13.86	523.45	10.48	1.322	4.27	3.60	3.49

Solution No.	Dilution and Amount of Acid Added	Gm. Cr_2O_3 per liter	CC. N/2 acid per liter	Gm. SO_3 per liter	$\frac{Cr_2O_3}{SO_3}$ (1)	Log. CH + immediately (2)*	Log. C_H+ after 3 days (3)*	Log. C_H+ after 50 days (4)*
11	25 cc. 21 + 0.0 cc. N/5 H_2SO_4 + 25.0 cc. H_2O	13.86	643.45	12.88	1.076	3.19	3.31	3.33
22	" " " " " 2.5 " " " " 22.5 " "	13.86	663.45	13.28	1.043	2.92	3.26	3.31
23	" " " " " 5.0 " " " " 20.0 " "	13.86	683.45	13.68	1.013	2.60	3.23	3.27
24	" " " " " 7.5 " " " " 17.5 " "	13.86	703.45	14.08	0.985	2.44	3.18	3.23
25	" " " " " 10.0 " " " " 15.0 " "	13.86	723.45	14.48	0.957	2.30	3.13	3.21
26	" " " " " 12.5 " " " " 12.5 " "	13.86	743.45	14.88	0.931	2.17	3.07	3.16
27	" " " " " 25.0 " " " " 0.0 " "	13.86	843.45	16.88	0.833	1.72	2.51	2.89

Solution No. 21 is No. 1 diluted 8⅓ times.

For accuracy in plotting the "basicity" value was calculated to three decimal places instead of to the customary two places.

* For value of Log. C_H+ in concentration of hydrogen ion in moles per liter see Table IV.

(1) Curve A, Fig. 3. (2) Curve B, Fig. 3. (3) Curve C, Fig. 3. (4) Curve D, Fig. 3.

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Effect of Added Acid and Alkali.

The values of the logarithms of the concentrations of hydrogen ion in Table III and the Curves B, C, and D, represent the change in concentration of hydrogen ion taking place in a stock chrome liquor when increasing amounts of acid and alkali are added. In Table V and the Curves F, G, and H, are the results of the duplicate experiments upon chromium sulphate.

TABLE IV.

Log. C_{H^+}	Conc. H^+ in mole per liter	Log. C_{H^+}	Conc. H^+ in mole per liter
1.72	0.01906	3.27	0.00054
2.17	0.00676	3.31	0.00049
2.30	0.00501	3.33	0.00047
2.44	0.00363	3.35	0.00045
2.51	0.00309	3.37	0.00043
2.60	0.00251	3.39	0.00041
2.89	0.00129	3.44	0.00036
2.92	0.00120	3.45	0.00035
3.07	0.00085	3.47	0.00034
3.13	0.00074	3.49	0.00032
3.16	0.00069	3.51	0.00031
3.18	0.00066	3.54	0.00029
3.19	0.00065	3.60	0.00025
3.21	0.00062	3.68	0.00021
3.23	0.00059	3.67	0.00011
3.26	0.00055	4.27	0.00005

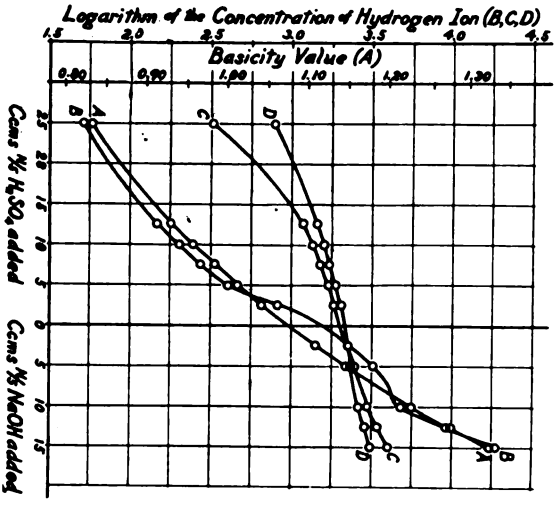

FIG. 3.—THE EFFECT OF ADDED ACID AND ALKALI UPON THE ACIDITY OF CHROME LIQUORS.

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TABLE V.—Effect of Added Acid and Alkali.

Chromium Sulphate Solution.

Solution No.	Dilution and Amount of Alkali Added	Gm. Cr_2O_3 per liter	cc. N/2 acid per liter	Gm. So_3 per liter	$\frac{Cr_2O_3}{SO_3}$	(1) Log. C_H+ immediately	(2)* Log. C_H+ after 6 days	(3)* Log. C_H+ after 30 days	(4)*
111	5.04 cc. 100 + H_2O to 50 cc.	13.86	897.1	17.96	0.770	2.43	2.33	2.42	
131	" " " " 2.5 cc. N/5 NaOH + H_2O to 50 cc.	13.86	877.1	17.56	0.789	3.04	2.50	2.51	
132	" " " " 5.0 " " " " " " " "	13.86	857.1	17.16	0.808	3.60	2.64	2.58	
133	" " " " 7.5 " " " " " " " "	13.86	837.1	16.76	0.827	3.92	2.75	2.63	
134	" " " " 10.0 " " " " " " " "	13.86	817.1	16.36	0.847	4.15	2.82	2.69	
135	" " " " 12.5 " " " " " " " "	13.86	797.1	15.96	0.868	4.29	2.86	2.72	
136	" " " " 15.0 " " " " " " " "	13.86	777.1	15.56	0.890	4.38	2.89	2.77	

Solution No.	Dilution and Amount of Acid Added	Gm. $Cr2O_3$ per liter	cc. N/2 acid per liter	Gm. SO_3 per liter	$\frac{Cr_2O_3}{SO_3}$	(1) Log. C_H+ immediately	(2)* Log. C_H+ after 6 days	(3)* Log. C_H+ after 30 days	(4)*
111	5.04 cc. 100 + H_2O to 50 cc.	13.86	897.1	17.96	0.770	2.43	2.33	2.42	
122	" " " " 2.5 cc. N/5 H_2SO_4 + H_2O to 50 cc.	13.86	917.1	18.36	0.755	2.15	2.18	2.36	
123	" " " " 5.0 " " " " " " " "	13 86	937.1	18.76	0.739	1.93	2.05	2.31	
125	" " " " 10.0 " " " " " " " "	13.86	977.1	19.56	0.708	1.66	1.88	2.16	
127	" " " " 15.0 " " " " " " " "	13.86	1097.1	21.96	0.631	1.31	1.54	1.69	

* For value of Log. C_H+ in concentration of hydrogen ion in moles per liter see Table VI.

(1) Curve E, Fig. 4. (2) Curve F, Fig. 4. (3) Curve G, Fig. 4. (4) Curve H, Fig. 4.

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TABLE VI.

Log. C_{H^+}	Conc. H^+ in mole per liter	Log. C_{H^+}	Conc. H^+ in mole per liter
1.31	0.04898	2.58	0.00263
1.54	0.02884	2.63	0.00234
1.66	0.02188	2.64	0.00229
1.69	0.02042	2.69	0.00204
1.88	0.01319	2.72	0.00191
1.93	0.01175	2.75	0.00178
2.05	0.00891	2.77	0.00170
2.15	0.00708	2.82	0.00151
2.16	0.00692	2.86	0.00138
2.18	0.00661	2.89	0.00129
2.31	0.00490	3.04	0.00091
2.33	0.00468	3.60	0.00025
2.36	0.00437	3.92	0.00012
2.42	0.00380	4.15	0.00007
2.43	0.00372	4.29	0.00005
2.50	0.00316	4.38	0.00004
2.51	0.00309		

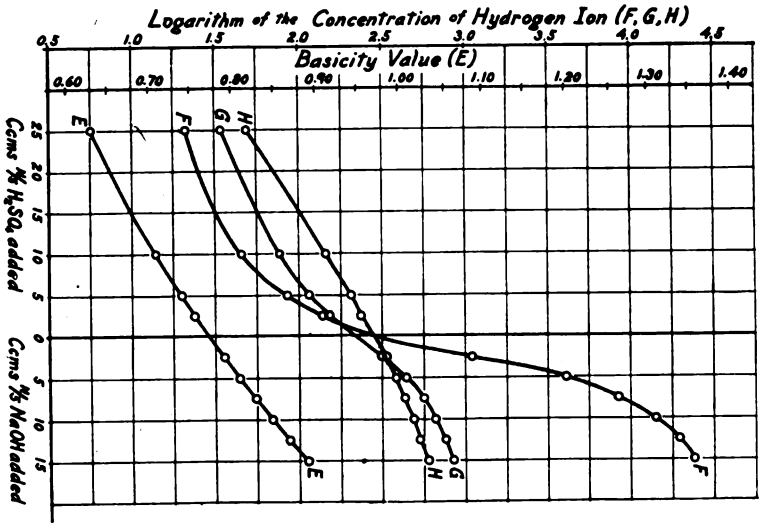

FIG. 4.—THE EFFECT OF ADDED ACID AND ALKALI UPON THE ACIDITY OF A CHROMIUM SULPHATE SOLUTION.

When the stock chrome liquor was diluted with standard alkali and water so as to contain 15 cc. N/5 NaOH in 50 cc. of solution, dilution number 11, and the hydrogen ion concentration determined immediately there were 0.00005 moles per liter. The

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"actual" acidity of this solution increased slowly, while standing, until, after 50 days, ionic equilibrium was reached at a concentration of 0.00032 moles per liter. When 25 cc. N/5 H_2SO_4 were contained in 50 cc. of chrome liquor, dilution number 11, and the concentration of hydrogen ion determined immediately there were 0.01906 moles per liter. The "actual" acidity of this solution finally reached equilibrium at 0.00129 moles per liter.

In the case of pure chromium sulphate the behavior is similar. When 15 cc. N/5 NaOH were contained in 50 cc. of chromium sulphate solution, dilution number 111, the hydrogen ion concentration, when determined immediately, was 0.00004 moles per liter. After standing 50 days this became 0.0017 moles per liter. When 25 cc. N/5 H_2SO_4 were contained in 50 cc. of chromium sulphate solution, dilution number 111, the hydrogen ion concentration when determined immediately, was 0.04898 moles per liter, while after 50 days it was 0.02042.

In these solutions the "basicity" value varied regularly with the amount of acid or alkali added, but here likewise it is not a measure of the "actual" hydrogen ion concentration. Moreover it is the same value whether determined immediately or after several days whereas the concentration of hydrogen ion is decidedly different.

The changes in "actual" acidity which the electrometric method has shown take place in a chrome liquor, upon dilution, and while standing after the addition of acid or alkali, are of such magnitude as to prove that the "basicity" value is too inadequate and misleading to be used as the only criterion of the tanning power of a chrome liquor and that accurate chemical control can be attained only after determinations of "actual" acidity have been made an essential part of the method of control.

We are indebted to Messrs. A. F. Gallun and Sons, of Milwaukee, for their generous support of this research, and to Mr. John Arthur Wilson for his helpful suggestions.

LABORATORY OF COLLOID CHEMISTRY,
Havemeyer Hall, Columbia University,
New York City. April, 1918.

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NOTES ON THE PROCTER-HIRST TEST FOR SULPHITE-CELLULOSE.

The following communication has been received by the editor.

Dear Sir:—

Some doubt has been occasioned in our minds, by the results obtained from the so-called Procter-Hirst test for sulphite-cellulose in the presence of natural tannins; it having been assumed by most leather chemists that the aniline-hydrochloric acid test is one which indicates, if positive, the presence of the sulphite-cellulose products.

Below you will find a tabulated statement, as to the actual results obtained by following the Procter-Hirst test on various materials:

Sumac extract (filtered)	No precipitate
Solid ordinary quebracho extract (filtered)	No precipitate
Treated quebracho	Slight precipitate
Chestnut extract No. 1 (filtered)	No precipitate
Chestnut extract No. 2	No precipitate
Spruce extract	Precipitate
Liquid muskegon extract (filtered)	Precipitate
Powdered muskegon extract (filtered)	Precipitate
Neradol A sulpho acid	Precipitate
Neradol B sulpho acid	Precipitate
Hemlock extract (filtered)	No precipitate
Oak extract (filtered)	No precipitate
Sulphite-cellulose liquor, specially treated	Precipitate

The only one that seemed in doubt, although it showed the characteristic tendencies to a slight degree, was the treated quebracho, which we have no doubt was sulphited. The reaction in this instance was very slight.

While the writers do not propose to state that lignones generally do not react to the Procter-Hirst test, it would seem apparent that this reaction was due to the presence of the SO_3 radicle in an organic complex, and does not make a differentiation between the organic bases.

We purpose to make further investigations along the lines of determining the actual cause of this reaction, if possible, but at

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the present we believe that naturally produced tannins do not react to the Procter-Hirst test, whereas practically all the products having the SO_3 radicle attached, do show this reaction.

Yours very truly,

JOHN H. YOCUM,
EMIL S. NELSON.

THE NOMENCLATURE USED IN COLLOID CHEMISTRY. A PLEA FOR REFORM.*

Colloid chemistry is no longer considered as a mere collection of mysterious substances and "abnormal" reactions. It is an important branch of chemical and physical science possessing a fairly well established working basis and is rapidly acquiring new students.

It suffers, however, like all virgin sciences, the affliction of superfluity of terms used to describe essentially the same things, careless and loose use of some expressions, and confusion of nomenclature in general. This condition results in a great handicap to new students. It is very difficult for them to acquire clear conceptions from their first readings of the various works on the subject.

It is time that this matter be taken in hand by some committee of our Chemical Society for the purpose of removing this needless handicap and confusion by defining the various terms used in colloid science, eliminating unnecessary ones and by standardization of the terminology in general, just as was done with the terminology of the proteins by the biological chemists some years ago.

The paragraphs which follow attempt to point out some of the cases of malusage of terms.

No objection can be raised against the word "colloid." It is distinctive, but the use of the expression "colloidal *solution*" is to be strongly condemned, since it is so evident that substances in the colloidal condition are not dissolved, in the strict sense of the term. Colloidal particles are in a condition midway between solution and mechanical suspension, and they are held in this pecu-

* *Science*, *N. S.*, Vol. XLVII., No. 1201, p. 10-14, January 4, 1918.

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liar state of *dispersion* by virtue of their surface energy, electrical charge, their kinetic energy as manifested by the Brownian movement, and the adsorbed ions of electrolytes which are essential to the stability of all colloids.

The general term "dispersion," as suggested by Wo. Ostwald, is to be preferred to the special term "solution," *e. g.*,

"Mechanical suspensions" are coarse dispersions,

"Colloidal solutions" are colloidal dispersions, and

"True solutions" are molecular dispersions.

The particles, or "internal phase" of these systems are known as the "dispersed phase," and the liquid in which they are dispersed, the external phase, is known as the "dispersion medium."

The present usage of the word "sol" and of its modifications—"hydrosol," "alcosol," etc., to describe a colloidal dispersion, is the same as that of Graham, their originator. I have noticed, however, that the word "sol" has been used by a few writers in the sense of the dispersed phase, *i. e.*, the particles in colloidal dispersion. Is this use of the term to be permitted? Graham invented it as a short and convenient substitute for colloidal "solution" and a perusal of the works by Bechhold, Cassuto, Freundlich, Hatchek, Ostwald, Taylor and Zsigmondy shows that the original sense of the expression has been retained by these writers.

The use of the term "gel," however, and of its modifications, "hydrogel," "alcogel," etc., is deplorably loose and confusing. This term was coined by Graham[1] and first used by him in discussing the "pectization" or coagulation of the hydrosol of silicic acid. Therefore, if we are to limit the use of "gel" to its original sense, we should use it only when speaking of the definite *coagula* of sols. This is not the case, however. Any substance which resembles a jelly in appearance is called "gel," although in chemical and physical properties it may be entirely different from the kind of matter which Graham had in mind when he invented the term. This use of the expression is exceedingly popular and would be very difficult to overcome.

Let us take up a case or two to show how unscientific this latter usage of the term is. For example, consider the dissolution or dispersion of gelatine in hot water. It forms a very mobile "solution" or rather dispersion, and in this form is called a hydrosol

[1] *Proc. Roy. Soc.*, 13, 337 (1864).

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or sol. If this hydrosol be allowed to cool, it becomes very viscous and "sets" to a jelly-like mass. In this stiffened form it is popularly known as a "hydrogel" or "gel." If it be warmed again its viscosity decreases, it becomes mobile and is called a "sol." Now if this use of the term "gel" (which is not as Graham intended) is to be permitted, then what is the line of demarcation between the sol and gel states? A change in state has occurred, it is true, for in the sol condition the water was the external phase whereas in the so-called gel state the gelatine became the external phase and the water internal. The change is very gradual, however, and our change of terms to suit the change in appearance of the system is exceedingly arbitrary and unscientific. Furthermore no chemical change in the nature of the gelatine has taken place.

If some alum or a trace of mercuric chloride be added to the gelatin hydrosol, a coagulum is obtained which is correctly termed a gel according to Graham. This is a coagulated compound, however, a chemical reaction has taken place. It will not redissolve in water and is, therefore, entirely different from the case discussed above, which is also commonly called gel.

To further complicate matters, the dry pieces of gelatine (and in fact any other colloid which will "dissolve" readily) which were used to make the original sol are also quite commonly called "gel." Lottermoser called attention to this several years ago and suggested that such pieces of gelatine, or of any other dry "soluble" colloid be called "solid sol." This suggestion is obviously bad. Why apply any special term at all?

When a hydrous ferric oxide sol is allowed to evaporate spontaneously, it will go through a jelly-like stage and finally become a hard scaly residue when all or nearly all of the water has left it. The jelly-like form will redisperse when warmed with an excess of water, while the amorphous form will not. Yet both forms are called "gel!" Zsigmondy distinguishes between these two different forms by calling the first one "hydrogel" and the second, "gel."

A review of the texts on colloidal chemistry shows the following conceptions of this term.

Cassuto[2] calls a gel the gelatinous precipitate obtained from a

[2] "Die Kolloide Zustand der Materie."

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sol by means of an electrolyte, heat or evaporation; *i. e.*, a gel is formed by coagulation of a sol. He calls stiffened sols (or jellies), "gelatines."

Bechhold[3] remarks the loose use of the word "gel" and states that he restricts it to the description of the coagula from sols. To the stiffened sols or jellies he applies the term "Gallerte," which in English might be called "jelly."

Freundlich[4] says that systems of solid dispersion media and liquid dispersed phase are gels as distinguished from the reverse which are suspensions or emulsions. In other words he applies the word "gel" to jellies.

Hatschek[5] refers to the fact that Graham applied the name "gels" to the products obtained by the coagulation of sols, but later on in his book he calls jellies, gels also.

Ostwald in his "Handbook of Colloid Chemistry," considers all colloids as gels when the system becomes "microscopically heterogeneous." That is to say, he applies the term promiscuously.

Taylor[6] uses "gel" in the same loose general manner as Ostwald, Hatschek and Freundlich.

Zsigmondy in his "Kolloidchemie," limits the word "gel" to the dry residue which will not redisperse in a solvent, but he applies "hydrogel" to the jelly-like mass formed by removal of the dispersion medium or by salt coagulation.

Hardy[7] recognized the difference in properties of substances called "gels" and he qualified the term—"gels by coagulation" and "gels by stiffening."

I feel confident that Graham did not apply this term as loosely as is popular at the present time. In his remarks on the properties of colloidal tungstic acid[8] he says: "It is remarkable that the purified acid is not pectized by acids or salts even at the boiling temperature. Evaporated to dryness, it forms vitreous scales, like gum or gelatine." Note that he describes the dry residue as "scales, like gum or gelatine" and not as gel.

[3] "Kolloide in Biologie und Medizin."

[4] "Kapillarchemie."

[5] "Introduction to the Physics and Chemistry of Colloids."

[6] "Chemistry of Colloids."

[7] *Z. physik. Chem.*, 33, 326; 385 (1900).

[8] *L. c.*, p. 340.

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It is evident, then, that the original meaning of the term gel has not been adhered to and in fact is more often applied to the state best described as jellies. Shall we adhere to Graham's definition or shall we discard it, restricting the term gel and its modifications to jellies, as popularity favors, and do away with any special terms to describe coagula from sols by electrolytes, or residues formed by evaporation to dryness? Special terms to describe these last two cases are obviously unnecessary and serve only to encumber colloid chemistry.

Lately the word "peptization" or "peptinization," as originated by Graham, has shown tendencies of wider use than formerly. Graham used this expression to describe the formation of a sol from a gel by the influence of a small amount of foreign reagent as, for example, the formation of a hydrous ferric oxide sol from a coagulum of ferric hydroxide by treatment with a small amount of hydrochloric acid or ferric chloride. He named it "peptization" because it resembled the hydrolysis of egg white to peptone by acid.

Cassuto, Hatschek, von Weimarn and Zsigmondy preserve the original sense of this term. Bancroft[9] has recently proposed, however, that we use peptization to describe all cases of transformation of gel (using this term in the present popular sense) to sol and not restrict it merely to cases where a foreign electrolyte has been added to accomplish the change; *e. g.*, when dry gelatine is "dissolved" in water Bancroft would call it a case of gelatine being peptized by water. This usage has its merits because it eliminates the word "dissolve" and the implication of "solution."

Ostwald defines peptization as the phenomenon opposed to coagulation.

Taylor prefers a new term, "solation," which he applies to all cases of gel ⟶ sol transformations, and incidentally he urges the adoption of "gelation" to define all cases of sol ⟶ gel transformations instead of coagulation or pectization.

"Pectization," another of Graham's terms, is rapidly dying out. The word "coagulation" covers all cases of pectization and therefore why preserve an unnecessary term? Furthermore, why adopt the new term "gelation" proposed by Taylor. "Coagula-

[9] *J. Phys. Chem.*, 20, 85-117 (1916).

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tion" is adequate. Of course, if it is decided to name jellies (stiffened sols) "gels," then the word "gelation" would be a good one to describe the "setting" of the gel or the stiffening of the sol.

Elimination of some synonymous terms is decidedly necessary from the list of names applied to the two more or less distinct classes or systems of colloid dispersions. For example, these two systems are variously named as follows:

The terms "emulsoid" and "suspensoid" are very popular. "Lyophilic" and "lyophobic" are very expressive. The "stable-unstable" and the "reversible-irreversible" terms should be abolished, since they describe the conduct and changes in state of colloids when subjected to external conditions and are not always sharply defined. For example, hydrous ferric oxide sol is fairly stable in the presence of neutral electrolyte (much more so than colloidal gold or platinum), while it is irreversible when evaporated to *dryness*. Most writers classify it with the suspensoids, although Taylor calls it an emulsoid (since if it be evaporated *not quite* to dryness it is partially reversible). In reality it belongs to neither of these two generally accepted classes; its properties place it midway between the two, nearer the suspensoid than the emulsoid class. All the hydrous oxides of the basic or acidic elements act similar to hydrous ferric oxide.

On account of this confusion of classification Bancroft[21] has suggested that the distinction between these two groups be done

Authors		
Noyes[10]	Colloidal solutions	Colloidal suspensions
Hardy,[11] Zsigmondy[12]	Reversible colloids	Irreversible colloids
Billitzer[13]	Baser colloids	Typical or genuine colloids
?	Hydrophilous colloids	Anhydrophilous colloids
Henri[14]	Stable colloids	Unstable colloids
Perrin, Freundlich,[15] Neumann[16]	Lyophilic colloids	Lyophobic colloids
Bary[17]	Dissolving colloids	Electrical colloids
Wo. Ostwald[18]	Emulsion colloids	Suspension colloids
von Weimarn[19]	Emulsoids	Suspensoids
Burton[20]	Gelatinizing type	Non-gelatinizing type

away with. He prefers to classify colloidal systems according as to whether water or the more mobile phase, is the internal or the external phase and states: "While we are reasonably sure that colloidal gold is a solid and that colloidal oil is a liquid, the two behave exactly alike when both are suspended electrically."

This suggestion is along the proper lines, but is too sweeping, since colloidal gold and colloidal oil do not behave alike.

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After a consideration of all the terms, it would seem that "lyophilic" and "lyophobic," or their more special derivatives, "hydrophobic" are the least objectionable terms, since most colloids answer to one of these designations. When our knowledge of colloids becomes exact enough to *sharply* differentiate between these two classes then we may find names for those systems which now seem to have properties which place them in neither of the above.

Before concluding, attention is directed to the irritating, although not very serious, mistake in the translations of the German terms "disperse" and "dispersions Mittel" by some authors. The German adjective "disperse" is "dispersed" in English, not "disperse," and "disperse Phase" is "dispersed phase," while "dispersions Mittel" is "dispersion medium" and not "dispersion means." These mistakes are like the old one of translating "Wanderung der Ionen" "wandering of the ions" instead of "migration of ions."

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[12] "Kolloidchemie."
[13] *Z. physik. Chem.*, 45, 307 (1903).
[14] *Z. physik. Chem.*, 51, 29 (1905).
[15] "Kapillarchemie."
[16] *Koll. Z.*, 3, 80 (1908).
[17] *J. Chim. Phys.*, 10, 437 (1912).
[18] "Handbook of Colloid Chemistry."
[19] "Grundzüge der Dispersoidchemie."
[20] "Physical Properties of Colloidal Solutions."
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ABSTRACTS.

Outline of Colloid Chemistry, II. W. D. BANCROFT. *Jour. Franklin Inst.*, **185**, 199-230 (1918); cf. this J., 13, 125 (1918). Part II of this paper is divided into thirteen parts and contains 146 references.

Adsorption from Solution by Solid.—In contact with a solution, a solid may adsorb the solvent and solute to different extents. This selective adsorption is exhibited by filter paper, which adsorbs numerous dissolved substances to a greater extent than it does water, so that dilute solutions of such substances as barium and calcium hydroxides should not be filtered if they are to be used in quantitative work.

The usual method for determining adsorption is to shake a known solution with a weighed amount of adsorbing solid, pipette off some of the supernatant liquid, analyze, and calculate the amount of adsorption from the decrease in concentration. Results by this method will be too low, if any of the solvent is adsorbed by the solid. Leighton tried to avoid this error, in his work on the adsorption of electrolytes by cotton, by centrifuging and then analyzing the cotton; but this method will give too high results unless all the unadsorbed solution is removed. With a solution of 200 grams NaOH per liter, Leighton found an adsorption of 0.27 gram NaOH per gram of cotton by the titration method and of 0.75 gram by his own gravimetric method, the true adsorption lying between these values.

Osaka's experiments on the adsorption of potassium and sodium salts by blood charcoal show that when allowance is made for the adsorbed water, adsorption is found to decrease in the order

$$I > NO_3 > Br > Cl > SO_4$$

the potassium salts being more strongly adsorbed than the corresponding salts of sodium. The selective nature of adsorption is shown by the fact that barium sulphate carries down large amounts of barium nitrate and only small quantities of barium chloride.

The Adsorption Isotherm.—An approximately quantitative expression for adsorption from solution is given by the equation

$$(x/m)^n = kc$$

where x is the amount of solute adsorbed by m units of the solid adsorbing agent, c is the concentration of the solution and n is a constant, not necessarily an integer, though experimentally never less than unity. Other formulas have been proposed or discussed by Freundlich, McBain, Schmidt, Georgievics, and others, but no formula is strictly accurate, and the simplest one seems best for the time being. If the curves really bend round parallel to the axis of ordinate, the simple formula is necessarily wrong.

Abnormal Adsorption.—Changes of adsorption have been observed in a number of cases due to flocculation or coarsening of the adsorbing medium. In the adsorption by silver iodide of dissolved potassium iodide, it has been noted that for concentrations up to about N/300 the expo-

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nential formula holds fairly well, but beyond this concentration the amount of adsorption actually decreases, the silver iodide becoming denser and more granular and showing signs of crystallization. On the other hand, silver nitrate is adsorbed by silver iodide without producing this change within the concentrations studied.

Osaka found that $NaNO_3$, KBr, KI, and KNO_3 are adsorbed positively by blood charcoal, while NaCl, Na_2SO_4, and K_2SO_4 are apparently adsorbed negatively, the solutions becoming more concentrated after being shaken with charcoal. Mathieu observed negative adsorption with a number of dilute solutions when adsorbed by capillary tubes. With normal solutions the concentrations in the capillary tubes were often only tenth-normal. The difference in concentration increases with decreasing radius of the capillary tubes and Mathieu considers it quite possible that with very fine tubes water alone would be adsorbed, a conclusion of distinct importance for the theory of semi-permeable membranes. It is clear that we get osmotic phenomena in two distinct ways depending upon whether we have a continuous film or a porous one. In the case of a continuous film it is essential that the solvent shall dissolve in the membrane and the solute shall not. With a porous film we get osmotic phenomena only in case the pore walls adsorb the pure solvent, and the diameter of the pores is so small that the adsorbed film of pure solvent fills the pores completely. Under these circumstances the dissolved substance cannot pass through the membrane unless adsorbed by the latter.

Reversibility of Equilibrium.—While the adsorption equilibrium is theoretically a reversible one, there are conditions under which there may be apparent or actual irreversibility. If charcoal takes a dye out of solution to such an extent as practically to decolorize the solution, no amount of washing with water will give a colored solution, even though dye is being taken out all the time. In this case the adsorption is strictly reversible, the difficulty lying in the interpretation of the results.

Specificity of Adsorption.—Adsorption is specific, the amount of adsorption varying with the nature of the adsorbing agent, the liquid, and the substance adsorbed. Charcoal and ferric oxide adsorb benzoic acid about ten times as strongly as acetic acid, while chromium oxide adsorbs the two acids about equally and platinum black adsorbs acetic acid a little, but benzoic acid practically not at all. Salts seem to show distinct adsorption for their own ions. Thus silver bromide adsorbs silver nitrate or potassium bromide, but not potassium nitrate. Charcoal adsorbs both acid and basic dyes; alumina readily takes up acid but not basic dyes; silica and tannin adsorb basic more readily than acid dyes. Wool adsorbs many dyes strongly without a mordant, but cotton relatively few.

In general an ion of higher valence is adsorbed more strongly than one of lower valence, but this is not invariably the case. Ions of the same valence may be adsorbed to quite different extents. Davis found that not only does charcoal adsorb iodine from different solvents to

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different extents, but the order of effectiveness for the solvents is not the same for different kinds of charcoal. At least two factors govern this effect of the solvent: the extent of adsorption of the solvent by the adsorbing agent and the solubility of the dissolved substance in the solvent, the greater the solubility of the substance, the less is adsorbed. In general the amount of adsorption is also decreased by rise of temperature.

Adsorption of Several Solutes.—Where two dissolved substances are present, it is usual to find that they will be adsorbed to different extents and that neither will be adsorbed to the same extent as when present alone. A substance which is more strongly adsorbed will usually displace one less strongly adsorbed.

Chemical Action.—Selective adsorption connotes the possibility of chemical decomposition as a result of adsorption. A neutral salt solution will become acid, if shaken with a solid which adsorbs the base more strongly than the acid, alkaline if the acid is more strongly adsorbed than the base, but will remain neutral if the extent of adsorption of acid and base is the same, which is due to the fact that all salts are hydrolyzed in aqueous solution to some extent, however small. An anion is more readily adsorbed in the presence of a readily adsorbed cation and a cation in the presence of a readily adsorbed anion. An acid dye will be taken up more readily in an acid than in a neutral solution and will be taken up least in alkaline solution. With basic dyes the reverse is true. Substances which poison catalysts are probably so strongly adsorbed by the catalysts that they prevent the adsorption of the reacting substances.

Adsorption from Solution by Liquid.—This is complicated by the possibility of the solute dissolving in the adsorbing liquid. Chloroform adsorbs hydroxyl ions from alkaline solutions, which accounts for the wetting of drops of chloroform by an alkaline solution.

Adsorption and Surface Tension.—The surface tension at a liquid-vapor surface is altered by dissolving a substance in the liquid, either increasing or decreasing. Since different solutions of the same density do not have the same surface tension, a hydrometer graduated for sulphuric acid solutions will not be accurate for hydrochloric acid solutions because the amounts of solution which will rise up the stem depend upon the surface tensions which are not the same in both cases. Changes in surface tension are accompanied by changes in concentration, the surface film of solution having a different concentration from the remaining mass, the rule being that the concentration in the surface film tends to change so as to decrease surface tension. Conditions at equilibrium are expressed mathematically by the equation

$$\Gamma = -\frac{da}{d\mu}$$

where a is the interfacial tension, μ the chemical potential of the dissolved substance in the aqueous phase, and Γ the mass of solute per unit area of interface (unspecified thickness) in excess of that corresponding to the concentration in the mass of the solution. This equation applies

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only to a substance really in solution, a point which is apt to be overlooked in papers on colloids. Such substances as soap, saponine, and gelatin are probably not soluble in water to any appreciable extent, but form colloidal solutions with surface tensions lower than that of pure water. In these cases the concentration of the added substance will be greater in the surface film than in the bulk of solution, but the Gibbs formula will not apply. As a matter of fact, the adsorptions in the surface are twenty to one hundred times those calculated from the formula with sodium glychocholate, Congo red, methyl orange, and sodium oleate.

From the fact that the lowering of the surface tension is accompanied by an increase in the concentration of the surface film of a true solution, Freundlich draws the conclusion that this is true in all cases, and that if a dissolved substance lowers the surface between the solid and the solution—whatever one may mean by that—the dissolved substance is adsorbed; conversely, that the dissolved substance is adsorbed only in case it lowers the surface tension at the interface. The conclusion may or may not be right, but the logic is faulty, because the two cases are not parallel. The Gibbs relation holds for a true solution, where the difference of concentration is entirely inside the solution phase. Freundlich is extending the relation to a heterogeneous system in which the adsorbed substance is presumably on the outer surface of the solid and by definition cannot diffuse into it, because we should then have a solid solution. It is very difficult to prove or disprove Freundlich's conclusion experimentally, but it is a great pity to have people believe, as many now do, that the generalization is based upon sound thermodynamics.

Brownian Movement.—The more finely divided a solid is, the more slowly will it sink to the bottom of a liquid, but extremely finely divided bodies apparently will not settle out in any finite length of time. Microscopic observations reveal that very small particles of any solid suspended in water exhibit irregular motions remarkably like those of bacteria. The view is taken that Brownian movements are due to the incessant bombardment by the molecules of the liquid; that the Brownian movements tend to make finely divided, suspended particles distribute themselves throughout the liquid; that the uniform distribution is affected by the force of gravity as in the case of a gas; and that the Brownian movements, though causing diffusion, give rise to no appreciable osmotic pressure. If enough of the particles coalesce, the force of gravity may cause the resulting mass to settle out.

Coalescence of Liquids.—Since two small drops of a pure liquid readily run together to form a larger drop, it is concluded that the larger drop is more stable than the two smaller ones. We should, therefore, expect small drops to distill over to, and condense upon, a larger drop, which is equivalent to saying that the greater the curvature of the drop, the higher its vapor pressure.

Coalescence of Solids.—Although not so apparent, the rule noted above for the coalescence of liquids applies also to solids. When enclosed in a container for a long time, very small crystals have been found to

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have been replaced by larger ones. A substance is more soluble, if extremely finely divided than when coarser. Two parts of a broken plate do not coalesce when pressed together because a film of condensed air prevents actual contact. Two pieces of platinum, however, may be welded together at a temperature far below the melting point.

Plasticity.—A plastic substance is one which can be moulded by pressure, which connotes that any break due to deformation is self-healing. A mobile liquid is not plastic because it will not retain its shape, but with increasing viscosity a liquid becomes plastic. In mixtures of solid and liquid, as the concentration of solid increases, there is a change from viscous flow to plastic flow. Bingham makes the distinction that with viscous flow, any shearing force, however small, will produce permanent deformation, whereas in the case of plastic flow, it is necessary to use a force of finite magnitude in order to produce a permanent deformation. It is reasonable to assume that zero fluidity corresponds to the point when liquid enough is present just to scatter the particles; *i. e.,* when enough liquid is added to fill the voids. J. A. W.

The Sulphonation of Fixed Oils. L. G. RADCLIFFE and S. MEDOFSKI. *Jour. Society of Dyers and Colorists.* Feb. 1918. The paper opens with a brief historical survey of Turkey red oils, their production, methods employed and uses; and a resumé of the various theories advanced as to the constitution of sulphonated oils, also extensive references to bibliography pertaining to all phases of the subject.

Radcliffe and Medofski studied the effect of sulphonation on various oils. The specific gravity, saponification value, acid value and iodine value were first obtained on the fixed oil. The fatty acids were then obtained by saponifying with alcoholic soda, dissolving the soap in boiling water, boiling off the alcohol, and liberating the fatty acids by the addition of HCl. The fatty acids were then washed with hot water to remove mineral acidity and the following constants of the resulting acids were determined: Solidification point (by titer test), iodine value, neutralization value from which the mean molecular weight of the acids was calculated, and the acetyl value.

The oils were sulphonated with different quantities of concentrated H_2SO_4, usually 100 grams of the oil with 35, 50 and 75 grams H_2SO_4. The oil was contained in a jar surrounded by ice water, the temperature in the experiments not being allowed to exceed 15° C. The H_2SO_4 was added drop by drop from a separating funnel and the mixture was kept agitated by an electrically driven stirrer. After all of the acid had been added the mixes were stirred 2 hours longer, after which the jars were corked and allowed to stand for some hours. The products were then washed with a saturated solution of Na_2SO_4 to remove excess of H_2SO_4. Finally the oils were heated in a water oven until they became clear. In some case, notably with sulphonated rape and linseed oils, this part of the treatment had to be eliminated because of charring and decomposition. The fatty acids were then prepared from the various sulphonated oils in

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the manner described above. The following constants were determined on these fatty acids: titer value, iodine value, neutralization value, saponification value and acetyl value.

The data for the various oils is tabulated and that of the fatty acids from the original oils and of those from the sulphonated oils are compared and interpreted as follows: An increase in the temperature of solidification and a corresponding decrease in the iodine value, which in most cases is very marked, shows that the H_2SO_4 has caused the formation of saturated solid compounds. The increase in the acetyl value indicates the formation of hydroxy compounds while the marked difference between the saponification value and the neutralization value of the fatty acids from the sulphonated oils shows the presence of lactones or anhydrides. Sesamé oil, cottonseed and olive oils, oleic acid, rape, whale, castor and linseed oils were studied in this manner.

The authors then studied the "power of oils to combine with H_2SO_4." About 5 grams of oil are accurately weighed into a small flask and a known quantity of concentrated H_2SO_4 is added under their conditions for sulphonation. After standing for 2 hours the mix is titrated with standard alkali. The acid values of the H_2SO_4 and of the oils and acids used are obtained and the difference between the number of milligrams of KOH, which would be required if no combination had taken place and that actually found, per gram of oil or acid taken gives a measure of the combining power of the oil with H_2SO_4 and is called the sulphonation number. They find that the combining power of oleic acid is greatest and decreases for oils with decrease in per cent. of oleic acid contained in the oils, while palmitic and stearic acids have the lowest values which are almost nil. They give rape oil as an exception, its "combining power" is high and its oleic acid content very low.

From these results, the acetyl value of the regenerated fatty acids and the iodine value of the original fatty acids of the various oils, the authors conclude that "the ease with which the H_2SO_4 acts upon oils and fatty acids depends not upon the 'degree of unsaturation' but upon the per cent. of olein or oleic acid present; also that the saturated acids have no action with H_2SO_4." As further proof of the latter statement pure tripalmitin was prepared and sulphonated in the usual manner when the palmitin appears to be regenerated unchanged. The very small decrease in titer test and a small increase in acid value showed that a certain amount of saponification had taken place. Pure myristic acid was also sulphonated with the same result.

An unsuccessful attempt to sulphonate Chinese wood oil (Tung oil) is recorded, also an attempt to prepare pure linoleic acid.

The authors summarize with their theory of sulphonation of oils as follows: "The data obtained show that the most easily sulphonated oils are those containing olein or oleic, and that the products of the reaction after saponification contain lactones or anhydrides and hydroxy acids.

"In the case of highly unsaturated oils, such as linseed oil, the action of H_2SO_4 is probably either to form unstable addition products (sulpho

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compounds) or to cause polymerization, the polymers also being easily broken down.

"With all of the oils, the H_2SO_4 acts to some extent (the amount is small at the low temperature employed in the sulphonations) as a saponifier, the glycerine being found in the mix, either in the free state or combined with the H_2SO_4 as sulpho-glycerine compounds."

G. W. S.

The Indian Hide and Leather Trade. SIR HENRY LEDGARD, *J. R. S. A.*, March 8, 1918. The author in a very comprehensive article describes the state of the trade. On the hide situation he speaks of the inferiority of the Indian oxhide, due to their heavy brands and cuts, and the hard work they must do.

When an animal is killed, or dies, immediate treatment to preserve the hide is necessary. In the central parts of India, the Bombay Presidency, the United Provinces, the Punjab and Sind, where a dry climate prevails, the hides are usually what is termed arsenicated, *i. e.*, they are cleaned of flesh, fat, etc., and sun or shade dried. Before baling for export they are dipped in a bath of arsenic solution and again dried. The arsenic acts as a preservative and prevents insects attacking the hides. This is considered the best method of treatment, as the hides keep well and there are not the opportunities for adulteration or weighting afforded by other cures.

In the damp climate of Bengal, and during the rainy season in other provinces, drying is difficult, so the hides are usually salted. The result is not always satisfactory; often a great deal of flesh and fat is left on the hide to absorb an excessive weight of salt. I have known a dry-salted hide weighing 15 pounds after the soaking in water, dissolving the salt, removing dirt, etc., which when again dried was found to weigh only 9 pounds, or a loss of 60 per cent. The purchase of salted hides on a weight basis under these circumstances is not satisfactory. For this reason, in the United Provinces, where dry arsenicated hides are usually sold per 20-pound weight, hides salted during the monsoon are valued by the piece, after selection and classification.

For many years the Indian Government purchased large numbers of cattle, kept them where troops were stationed, fed them well for about three months, and then slaughtered them to supply beef to the British soldier. The hides from these, known as "Commissariats," were sold by public tender for a year to three years in advance, and these were the best in India. They were branded on the neck with the letter "C," and a number corresponding with the month when bought, and realized the highest prices. Many years ago the Indian Government discontinued buying cattle, but this term "Commissariat" remains in the trade and indicates the highest grade of hide. The next grade, known as "Slaughtered," signified that the hides were from slaughtered animals as distinguished from those which have died a natural death. The third grade was termed "Deads;" and still lower are "Rejections." These trade terms

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are still used by the chief hide markets in the central parts of India, the Central Provinces and the Punjab—though the classification has changed. For instance, Commissariat, though non-existent, still represents the best hides, and "Slaughtered" include the next lower grade of slaughtered hides and the best of those from animals that have died. The hides of Bengal, Maherpore, Chittagong and other districts have each their distinctive characteristics and are classified accordingly.

Of goatskins there are in India several varieties. The best are from the Province of Behar and known as "Patnas." They are fine in grain, and ideal for the production of glacé kid skins. Further east, in Dinagepore, Bengal and Eastern Bengal (including Dacca), the skins are somewhat larger and heavier in grain and texture, but still suitable for glacé kid. Passing westward into the United Provinces and Rajputana we find the skins also larger and rather coarser than Patnas, the lighter ones only of value for glacé kid. The heavier are suitable for "Moroccos" for the upholstery trade, but unfortunately, many have holes made by the pricks of thorns on trees where the animals feed. Further north in the Punjab the skins are known as "Amritsars." They are large, strong and heavy, and best adapted for upholstery. In the south, Hyderabad and Deccani skins are of fair quality, chiefly purchased by the Madras tanners, and tanned in Southern India.

A great many hides are tanned annually in India.

"The primary processes, *i. e.*, softening, liming, unhairing, fleshing and bating generally, resemble the methods which obtained in England until the introduction of labor-saving machinery. In India, where labor is relatively plentiful and cheap, the Indian tanner still adheres to the more primitive methods.

The tanning material chiefly used in Madras and Bombay is the bark of the *Cassia Auriculata* shrub, commonly known as tarwad. It grows to about 6 to 8 feet in height, and has no trunk, the shoots breaking out a little above the ground. Shrubs of three to four years' growth are cut and the bark removed. Fresh shoots grow and are again ripe for cutting in about three to four years. Trees are usually destroyed when bark is taken from them for tanning purposes, so in this respect there is a distinct advantage in the use of tarwad.

No tanning material more suitable than tarwad where softness and pliability in the leather are desired is known by the author.

In the Bombay and Madras Presidencies it is the practice only partially to tan the hides, about half tanned according to our Western ideas; no exception is, however, taken to this as the European currier is able to complete the tanning to suit his requirements. There are some large and up-to-date tanneries at Cawnpore. The tanning materials used here are the *Acacia Arabica* or babul and the *Terminalia Chebula* or myrobalan nut.

For firm leathers babul tannage is very suitable, and when toned with other tanning materials can be used for upper leather. Chrome tanning is carried on to a very limited extent.

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Owing to the great impetus given by the war to tanning, the cutting of tarwad has been very much increased, and there has been a considerable rise in price. In the north, the Cawnpore tanneries have year by year to go further afield in search of babul. Neither of these two tanning agents, so important to the industry, are systematically cultivated. Tarwad is a jungle plant, flourishing in the central parts of India. Babul, a tree scattered over a wide area, chiefly in the northern parts of India, is not ripe for cutting until ten to twelve years old.

Private enterprise will not cultivate the babul tree and wait so many years for a return, nor has any enterprising Indian tanner taken in hand the plantation cultivation of tarwad. It is obviously the business of the Indian Forest Department, and it is trusted the Government of India will realize the importance of the tanning industry, and assure to it an ample supply of tanning. India can produce the bark, but its exploitation should not be left to private enterprise.

In addition to the tanning centers of Bombay, Madras, and Cawnpore, there still exists, mainly to supply the local needs of the districts, the primitive system commonly known as "country tanning," carried on in the villages. The hides and skins, after the usual preparation, are sewn into a bag, hung up, and filled with water and ground bark. The liquid extract percolates through the hide; 24 hours' suspension in the case of cowhides, and 48 with buffalo, completes the process. The hides are colored and look tanned, but a true chemical combination has not taken place. That they are not properly tanned is indicated by the unpleasant smell they give off for a long time. This leather comes to London from time to time in small quantities, where it is known and sold as "stitched hides," or "bag tanned."

Of the three centers of tanning reviewed, the Madras and Bombay *Cassia Auriculata* tannage is the largest, and meets an important demand in Europe. The second is a sound tannage, but has a limited market. The third is inferior, only of value where better leather is not available, and will die out as the better tannages find a wider market in India.

The Properties of Fat in Leather. W. FAHRION. *Chem. Umschau*, 1917, 29; abstract through *Coll.*, 1917, 325; *J. S. L. T. C.*, Feb., 1918. The spued fat and the fat still in the leather were separated from pieces of leather which had spued very badly. The two samples of fat were examined as regards color, melting point, crystalline structure, fatty acids, and the color, melting point, crystalline structure, molecular weight and iodine value were also determined for the fatty acids. The acid value of the speud fat was found to be lower than that of the residual fat in the leather so that the spue does not necessarily consist of free fatty acids. The spue was brighter in color, more of a crystalline nature, possessed a higher melting point and lower iodine value than the residual fat in the leather. This indicates that spueing arises from fractional crystallization of the more saturated solid fatty acids. With due reservations the author advances the theory that there is danger of spueing in the case of those

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fat-liquored or curried leathers which have been treated with a mixture of glycerides from which a different mixture of glycerides of low melting point and high content of saturated fatty acids can be fractionally separated.

Iron Tanned Leather. *Der Gerber*, 1916, 1010, 1012; 1917, 1016; through *Coll.*, 569, 341; *J. S. L. T. C.*, Feb., 1918. Dr. Bystron and Dr. Karl Baron have been granted several patents for iron tannages, according to which a 10° Bé. ferrous sulphate solution is oxidized by means of a slow current of nitrogen peroxide or a mixture of peroxide and oxide. The peroxide is obtained in the liquefied condition or by decomposing nitrites. In practice, ½-1 per cent. alkali nitrite and 5-10 per cent. neutral salt of an alkali are added to the ferrous sulphate solution together with the necessary amount of sulphuric acid to decompose the nitrite. The pelts are drummed in this solution. By passing air into the drum the reduced peroxide can be regenerated and further oxidation of the iron salt ensues.

When the leather is tanned through it is freed from excess iron salt by washing with solutions of neutral alkali salts, which remove excessively acid salts and precipitate the strongly basic tanning compounds of iron. Thus detrimental iron compounds are removed without at the same time detannizing the leather which usually happens when the washing is carried out with water alone or with alkalies. By repeated treatment with solutions of neutral alkali salts the leather can be freed from the last trace of acid iron salt, and hence the finished leather can be stored without deterioration due to the grain becoming brittle. Sodium sulphate is the best salt to use in this washing process.

Bystron and Vietinghoff have produced sole leather by this process. The product "Ferroxleather" by name, closely resembles the vegetable tanned leather, has a reddish-yellow cut, and gives the following results on analysis:—

	Per cent.
Water	13.02
Ash	14.91
Fat	2.61
SO_3	18.97
Hide substance	55.71 (9.91 per cent. N)

The excess of 5 per cent. may be due to a wrong conversion figure for the nitrogen or possibly to oxidation in estimating the sulphuric acid.

Dr. Otto Röhm has marketed an iron compound called "Ferreon" for tanning purposes. The properties of his iron leather are intermediate between those of chrome and vegetable tannages. The leather has a tough grain, a reddish-yellow color, gives a deep black with logwood, and can be used for the most varied purposes from gloving to boot soles.

Stefan Begony offers a very simple process for iron tanning. Pickled pelts prepared exactly as for chrome tannage are paddled or drummed in a solution of green vitriol mixed with acetic acid, until penetrated. The

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drained pelts are next treated with a soda solution, hung up to dry and washed to remove soluble salts. Thus tanned, the skins permit of a beautiful finish, will take up grease, and can be dyed.

The Detection of Tannins by the Formaldehyde Precipitation Method. R. LAUFFMANN. *Coll.*, 1917, 322; *J. S. L. T. C.* Feb. 1918. The author has determined the percentage total solubles and percentage tans precipitated in the Stiasny formaldehyde-hydrochloric acid reaction, for different tanning materials, extracts and mixtures of extracts, with a view to determining the characteristic figures for the different materials. It was hoped that these figures would have afforded a new method of tannin identification.

	Per cent. total sols pptd. by HCHO-HCl.	Per cent. tans pptd. by HCHO-HCl.
Pine bark	59—65	92— 99
Pine bark extract	40—49	66— 80
Oak bark	61—80	82—101
Oak bark extract	42—62	64— 89
Oak wood	20—30	26— 36
Oak wood extract	12—19	17— 26
Queb. extract	94—96	105—107
4 pts. Oak bark ext. / 1 pt. Queb. ext.	62 (Calc. 55)	82 (Calc. 74).
4 pts. Oak bark ext. / 1 pt. Pine bark ext.	50 (Calc. 47) / 62 (Calc. 60)	72 (Calc. 67). / 87 (Calc. 85).

Although both quebracho extract and pine bark extract are pure catechol tans and as such should be completely precipitated, they give different precipitation figures. The higher figure with quebracho extract cannot be attributed to simultaneous precipitation of non-tans, since its non-tan content is so small. It must be due to the tannins in the two extracts being of fundamentally different constitution. Pine bark figures are very close to those of oak bark extract. The former should be completely precipitated and the high figures with the latter may be due to simultaneous precipitation of some of the pyrogallol tan or to different constitution of the two tannins.

The figures obtained with extracts are appreciably lower than those of the respective materials. This indicates that tannin extraction or the decolorizing and clarifying of extracts partially removes the substances forming insoluble products with formaldehyde or it partially transforms them into such compounds as do not give an insoluble condensation product with formaldehyde.

The precipitation figures vary within rather wide limits for the same material and are 4 per cent. higher with mixtures than would be anticipated by calculation. The experiments show that with the tanning materials and extracts used, the formaldehyde precipitation figures can only have a very limited sphere of usefulness for identifying tannins, but they

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are useful in many cases, taken in conjunction with the results of other methods of testing tannins for identification purposes.

The Estimation of Chromium in Chrome Salts, Liquors, Leather Ashes and Residues. K. SCHORLEMMER, *Coll.*, 1917, 345 and 371; *J. S. L. T. C.*, Feb., 1918. The gravimetric estimation of chromium is involved, inaccurate, and takes up much time. The chromium hydroxide always carries down with it some of the soluble alkali salts present; these are very difficult to remove by washing, in fact, traces always remain and form chromate on igniting the hydroxide. Chromium estimations should only be done volumetrically. The chromic salts should be oxidized to chromates either with sodium peroxide or alkali and hydrogen peroxide. The author recommends the latter method. He finds that with iron-free chrome salts, the oxidized solution is reduced by acidifying. He thinks this is due to some hydrogen peroxide always remaining in an iron-free solution, whereas a trace of iron salt functions as a catalyst facilitating the oxidization and hastening the decomposition of the excess peroxide.

The oxidized chromium salt can be estimated by

I. Adding potassium iodide, acidifying and titrating with standard thiosulphate.

II. Adding excess of N/10 ferrous ammonium sulphate and determining excess by means of standard permanganate.

III. Titrating with N/10 ferrous ammonium sulphate and determining end point by spotting on a tile with potassium ferricyanide.

The first is the simplest, quickest and most accurate, but it is rather costly. The permanganate method is fairly exact but the decomposition of the permanganate solution necessitates frequent testing of it against the iron solution. The third method is simple in practice, but it requires more time and is not so accurate.

The above methods are only suitable for chrome salts and liquors. Chromium in leather ashes must be converted into chromate by fusion with magnesia and sodium carbonate. In the case of chrome liquors containing impurities such as organic matter, dyestuffs, etc., the oxidation cannot be effected by means of peroxide solutions. The solution must be rendered alkaline with caustic soda, treated with concentrated permanganate solution and boiled. The reddish-violet color of the permanganate disappears on boiling and more permanganate must be added and the solution boiled again. This process is repeated until the red color finally persists even after boiling. The small excess of permanganate is removed by warming the solution with two drops of alcohol. The solution is filtered, the filter well washed, and the chromium determined in the filtrate by one of the above methods.

The author has verified the work of Lamb and Harvey on the effect of iron on the determination of chromium in leather ash. He points out that any iron present with the chromium will not affect the result if the ferrous ammonium sulphate method is employed. He suggests that the

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chromium in the solution should be estimated by Methods I. and III. Where iron is present Method I gives a higher result. The lower figure should not be regarded as the correct estimate, but the solution should be freed from iron and the chromium should be re-determined by both methods. The figures now obtained should agree and they represent the true chromium content of the solution. Very often these agree with the result obtained with Method III. on the solution containing iron. The author has noticed many instances where this is not the case and these are at present under further investigation.

Critical Examination of Tanning Materials, Extracts, Chrome Liquors and Leathers. R. LAUFFMANN. *Coll.*, 1917, 377. *Tanning Materials and Extracts; J. S. L. T. C.*, Feb., 1918. After giving detailed methods of estimating sand and iron in ground tanning materials the author proceeds with his review. The value of tanning materials and extracts depends not only on the tannin content, but also on the proportion of tans to non-tans, and in the case of extracts on the degree of clarification and decolorization. Badly clarified extracts reveal an appreciable content of insolubles on analysis and these separate out in fairly strong solutions, as used in practice. Liquors made from such extracts must be clarified by settling before use, otherwise the insolubles will choke the pores of the hide resulting in a slow poor tannage and an inferior product. Many German war-time extracts either cannot be clarified by settling or take a very long time and they are not very useful for tanning purposes. The official method for estimating insolubles is not a suitable criterion for practical purposes since the liquors in practice are very much stronger. Paessler and Keit's method (*Coll.*, 1908, 295) is much more adapted to practical strengths. A good test consists in diluting 20 parts extract with 80 parts water in a 100 cc. measuring cylinder and allowing to stand overnight. Tanning extracts of suitable quality should give no precipitate or at most only a few cubic centermeters while the supernatant liquor should be as clear as possible, otherwise it will be very difficult to clarify the liquors in practice.

For comparative color tests the Lovibond tintometer is recommended for liquors, and tanning tests with calf or hide split for the color of the tanned leather. Insufficiently clarified or decolorized extracts give a badly colored tannage. This tanned leather can be used to determine the influence of light on the color (*Coll.*, 1912, 265). The tanning of the hide or calf piece will also give some indication of the speed and degree of tannage given by the particular extract.

Sulphited extract can be detected by the smell of sulphur dioxide on warming a little diluted extract with acid, or by means of lead or iodate starch paper. To estimate the sulphite two determinations must be made. The sulphites in a weighed quantity of extract must be first decomposed, the sulphur dioxide expelled, and the sulphuric acid estimated in the residue. Secondly, the sulphites in a fresh portion must be oxidized and

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the sulphuric acid again estimated. The difference gives the sulphites as sulphuric acid.

The total sugary matter should be determined by von Schroeder's method. The addition of glucose to the extract can only be assumed from this result if it is greatly in excess of the normal sugar content of that material and if the sugar content appears very high compared to the other non-tans.

Magnesium sulphate and other mineral products are estimated in the usual way. Details of the ordinary analytical procedure with chrome liquors are provided. With regard to vegetable tanned leathers, more than 2 per cent. sugary matter points to adulteration, as also does an ash exceeding 1.5 per cent.

The Estimation of Iron in Lactic Acid. A. HARVEY. *J. S. L. T. C.*, Feb., 1918. The author calls attention to the fact that none of the articles or methods published by the A. L. C. A. has considered the determination of the iron present

In a colorimetric method potassium sulphocyanide will not work in the presence of lactic acid. The author proposes a method using potassium ferrocyanide as an indicator in its place.

The method now suggested is as follows:—25 cc. of the sample are diluted to 500 cc. in a graduated flask and 25 cc. of this solution pipetted into a "Nessler" glass, such as is used for the estimation of ammonia in water, and diluted to 100 cc. One cc. of a 10 per cent. solution of potassium ferrocyanide is added, and the solution allowed to stand for about 3 minutes, in order that the color may develop. The tint is now matched against a series of standard colors produced from known volumes of the standard iron solution—previously diluted to 100 cc. and treated with 1 cc. of 10 per cent. potassium ferrocyanide. These should be made up at the time of the experiment so as to ensure uniformity of conditions.

The standard iron solution used was made by oxidizing 0.7 gram of pure ferrous ammonium sulphate with a small quantity of nitric acid and the solution made up to 1,000 cc. with distilled water.

In examining the very dark samples which are sometimes met with, it was found that the colored organic matter present interfered somewhat with the estimation. With such samples this method cannot be applied.

Treatment of Anthrax. G. D. DUDLEY, *J. A. M. A.*, Jan. 5, 1918. The author gives an excellent description of localized anthrax infection as it gradually develops. He states that anthrax is seldom fatal. When treated properly, few, if any, patients die. Three methods of treatment are described: 1. By excision after previous treatment with 8 per cent. phenol, afterwards painting with pure phenol, followed by absolute alcohol and a wet dressing. 2. When excision fails, injecting more 8 per cent. phenol, and incising freely, inserting gauze drains and applying an ice bag. 3. Use of anti-anthrax serum prepared by the U. S. Bureau of Animal Husbandry. Stimulating treatment is used in conjunction.

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Sampling Coal for Analysis. GEORGE S. POPE. Technical Paper 133, Bureau of Mines, U. S. Dept. of the Interior. The author in this paper shows the importance of proper sampling and gives very detailed instructions how the proper sampling should be done.

Production of Substitute Soles in Germany. *Commerce Reports.* The supply of substitute soles in Germany is controlled by the Soling Substitutes Co., which in turn is subordinate to the Imperial Ministry of Economics. The decision as to what kinds of soles not wholly of leather in a single piece, what kinds of preservers and protector made partly of leather, and what kinds of leather substitutes may be produced rests with the Soling Substitutes Co. There are now, says the Hamburgischer Correspondent, about twenty-five firms engaged in the manufacture of substitute material for soles. It is estimated that these firms can turn out soles for 100,000,000 pairs of boots per annum.

From January to September, 1917, there were produced soles (including flexible half-soles) for 1,000,000 pairs of footwear; uppers of paper cloth for the same number; toe-caps for 8,500,000 pairs; and inner soles for 500,000 pairs. During the next three months (October-December) it was expected that the output would be 10,000,000 pairs of uppers and 5,500,000 pairs of toe-caps and inner soles, all for new footwear. From January to September, 1917, 14,500,000 pairs of substitute soles for the repair of footwear were disposed of by the Soling Substitutes Co., and 4,000,000 pairs (chiefly of wood) in the open market. The supply for the period October to December is estimated at 24,000,000 pairs. In connection with the manufacture of half-wood soles, which are disposed of in the open market with the permission of the Soling Substitutes Co., sixty-five firms are engaged, with a weekly output of 1,000,000 pairs.

There are one hundred eighty firms employed in the manufacture of whole-wood soles for new footwear, with an average weekly output of 400,000 pairs. From January to September, 1917, there were sold, roughly, 8,000,000 pairs of soles made entirely of wood. Beech wood has been chiefly used, but any other hardwood, with the exception of oak, would serve equally well. The consumption of wood for soles in the period from January to September was about 63,000 cubic meters [cubic meter = 35.314 cubic feet]. The Soling Substitutes Co. proposes to deal with no less an amount than 600,000 cubic meters during 1918.

Of the boot and shoe factories which were in existence before the war only about 400 are now at work; of these 25 per cent. are working for the army administration alone, 25 per cent. are employed in connection with the manufacture of gloves and similar articles, and the remaining 50 per cent. have the task of meeting the civilian boot and shoe requirements.

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PATENTS.

Bark Peeling Machine. U. S. Patent 1,254,362. P. C. SCHAANNING, Christiana, Norway.

Tanning Compound. U. S. Patent 1,254,364. O. SCHMIDT and A. ANDRES, Germany, assigned to Badische. The process and product, when phenolic bodies, sulphuric acid and an aldehyde or phenol, paraldehyde and sulphuric acid, are made to react together.

Machine for Bending Leather Edgewise. U. S. Patent 1,255,366. JOHN N. WEIMER, Indianapolis, Ind.

Leather Stamping Machine. U. S. Patent 1,256,351. B. J. MILLER, Milwaukee, Wis.

Tanning. U. S. Patent 1,256,718. R. N. MOORE, Thorp Spring, Texas. A tanning solution composed of 2 pounds of gum gambier, 1 pound of Epsom salts, 1 pound of pulverized alum, 1 pound nitrate of soda, and water.

Tanning. U. S. Patent 1,256,789. LEWIS T. HALL, Houston Heights, Texas. Hides are tanned in an infusion of tillandsia (southern moss).

Tanning Fish Skins. U. S. Patent 1,256,974. K. BENDIXEN, Copenhagen, Denmark. The process consists of soaking in a solution of arsenic and sodium sulphide for three days; then liming three days, bating, pickling and tanning with sumac.

Utilizing Waste Leather. U. S. Patent 1,257,025. MARTIN REICHMAN, Germany. The leather is cut to pieces of equal size; threaded on wires into bands, and such bands interwoven one with the other.

Leather Softener. U. S. Patent 1,257,355. K. H. HUNTER, Great Bend, Pa. A mixture consisting of 74 parts first press moellon, 25 parts vacuum oil, 15 parts wool grease, and 30 parts of an aqueous solution having 7 pounds of soap and 7 pounds of soda to each 150 gallons of water.

Softening Hides. U. S. Patent 1,257,402. OTTO RÖHM, Darmstadt, Germany. Consists in treating the hides in a solution of the fat and albumen dissolving enzyms of the pancreatic glands (about 0.05 per cent. pancreatin) with or without 1 per cent. soda ash.

Machine for Finishing Leather. U. S. Patent 1,257,595. J. U. FLANAGAN, assignor to F. F. Slocomb & Co., Wilmington, Del.

Leather Treating Composition. U. S. Patent 1,258,729. J. F. WINNEUR, Rochester, N. Y. A mixture of approximately 400 parts of kerosene, 3 parts sassafras oil, 64 parts citronella oil, 1 part wintergreen oil, 1 part mirbane oil, 1 part birch oil and 46 parts raw linseed oil.

Reinforced Leather. U. S. Patent 1,259,180. M. W. WHITE, Cliftondale, Mass., assignor to U. S. M. Co.

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Leather Dampening Machine. U. S. Patent 1,259,199. E. B. AYRES, assignor to Philadelphia Textile Mach. Co.

Leather Whitening and Buffing Machine, U. S. Patent 1,260,436. T. J. O. KEEFFE, Cambridge, Mass.

Leather. British Patent 110,750. O. RÖHM, Germany. Skins are tanned with an aluminium salt of a lower fatty acid (formic or acetic).

Oxalic Acid. British Patent 110,837. ALLEN BROS. & CO., London. Oxalic acid and oxalates are obtained from "sal bark" (the bark of *shorea robusta*). After leaching out the tannins, the bark is treated with a mineral acid to break up the calcium oxalate contained therein, and the liberated oxalic acid recovered. The bark can then be used for paper making by treatment with an alkali.

Tanning Compound. British Patent 111,141. J. Y. JOHNSON, London, assignor to Badische. Practically same as U. S. Patent 1,254,364 (see above).

Leather. British Patent 111,304. W. C. BLATZ, Wilmington, Delaware. White leather is made by filling the skin with an insoluble white salt of one of the alkaline earths, preferably barium sulphate, during or subsequent to the process of tanning or tawing. This can be done by dipping alternately in barium chloride and sodium sulphate.

Purifying Sulphite-cellulose Liquor. British Patent 112,395. A. G. BLIXAM, London. Treatment with an alkali carbonate followed by sulphuric acid.

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FIFTEENTH ANNUAL MEETING.

The fifteenth annual meeting of the American Leather Chemists Association was held in conjunction with the semi-annual meeting of The National Association of Tanners at Atlantic City, May 15, 16, 17 and 18th.

The following organizations also participated in the meetings of The National Association of Tanners:

Tanners Council.

Morocco Manufacturers' National Association.

Patent and Enameled Leather Manufacturers' Association.

National Association of Importers of Hides and Skins.

The chemists' meeting, opened Thursday, May 16th with an address by the president of the Association, Mr. C. R. Oberfell. This was followed by the report of the secretary and treasurer, Mr. H. C. Reed. Mr. J. S. Rogers then gave his committee report on "The Determination of Free Sulphuric Acid in Leather," which was followed by considerable discussion. The meeting then adjourned for a joint luncheon with all participating organizations present. After the luncheon the following program was held:

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TOAST

"The President of the United States".....MR. C. F. C. STOUT
Chairman, Hide and Leather Control Board.

"FOREIGN TRADE DEVELOPMENT."

1. "Export Trade and the Webb-Pomerene Law"
PROFESSOR LINCOLN HUTCHINSON, War Industries Board
2. "Practical Handling of Foreign Trade."
MR. STANLEY H. ROSE, *Manager Foreign Sales*, The Barber Asphalt Paving Company.
3. "Selling Heavy Leather Abroad"
MR. E. G. HOWES, Howes Bros. Co.

On Friday, May 17th, a joint meeting was held, the program being arranged so as to be of special interest to the tanners present.

In the morning session the president first introduced Mr. J. B. Churchill of the American Leather Research Laboratory to the members. Mr. Churchill gave a brief talk expressing his appreciation of the help given him by the tanners and chemists and asking for their continued co-operation and assistance.

Mr. F. H. Small then read a very comprehensive paper on "Problems for the Consideration of the American Leather Research Laboratory." Mr. Fred A. Vogel then read a paper on "Upper Leather for Army Shoes."

Major Kenneth A. Marlatt of the Canadian Army then gave a very interesting talk on "Boots and Shoes Under Actual Trench Conditions" and also a few of his experiences and observations on the war in general. In the afternoon, papers were read by Dr. Allen Rogers on "Shoe Leather for Army Shoes;" by P. L. Wormley on "The Work of the Bureau of Standards in Leather," and by C. L. Peck on "The Profitable Recovery of Proteids from Tannery Waste Water." All these papers were followed by considerable discussion.

The program continued Saturday morning, May 18th.

Messrs. H. R. Davies, C. R. Delaney, T. A. Faust, R. W. Griffith and T. G. Greaves presented reports on their respective committee work A paper by Messrs. F. P. Veitch and R. W. Frey on "The Preparation of Heavy Leather Samples for Analysis," was read.

In the executive session following it was voted that the sum

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of $250.00 be given from the funds of the Association to The National Red Cross.

The convention concluded with the election of officers.

The following were chosen to serve for the next two years:

President, R. W. GRIFFITH.
Vice-President, W. K. ALSOP.
Secretary-Treasurer, H. C. REED.
Council, J. S. ROGERS, C. C. SMOOT, III.

All committee reports, papers and addresses presented at the convention will be published in subsequent issues of this JOURNAL. The paper by Mr. Small and the paper by Messrs. Veitch and Frey are to be found in this issue.

PREPARATION OF HEAVY LEATHER SAMPLES FOR ANALYSIS.*[1]

By F. P. Veitch and R. W. Frey.

Although the preparation of samples is known to be a factor of the utmost importance in the correct analysis of leathers, very little has been published concerning the subject. The variations in results which may occur and the need of a standard method of preparing leather samples are clearly shown by the results which follow.

It developed upon inquiry among several of the leather chemists that numerous means, among which may be mentioned chopping, clipping, rasping, planing, grinding in a coffee mill, and shredding by saws, are resorted to in the preparation of leather samples. This state of affairs is certainly not conducive to uniformity and to agreement between laboratories, to say nothing of the possibility of an injurious effect of some of the methods on the sample giving rise to erroneous results on analysis.

Of the various procedures named above the one which probably appeals the strongest for the preparation of samples of heavy

* It is desired to acknowledge the assistance in the analytical work of Mr. I. D. Clarke.

[1] Read at the Atlantic City meeting of the A. L. C. A., May 18, 1918.

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leathers, not only because of the ease and speed, but also because of the excellent state of division in which the sample is obtained, is that of shredding by means of a circular saw apparatus, which consists in general of three or four circular saws mounted, with their teeth staggered, on a shaft. The saws are revolved and the leather is shredded by feeding it against them.

Just after the installation in this laboratory of a circular saw machine, attention was called by an experienced chemist, through correspondence, to the fact that he had found decided differences between the moisture and soluble solids of the same leather when planed and when sawed.

The planed sample, despite its comparative coarseness, always gave the higher results on both constituents. Several samples were immediately prepared in this laboratory both by planing and sawing and determination of moisture and soluble solids confirmed this statement as shown in Table I.

TABLE I.

L. & P. No.	Preparation	Moisture per cent.	Soluble solids per cent.
34008	Sawed	4.9	22.0
34008	Planed	10.4	26.5
34014	Sawed	6.4	17.7
34014	Planed	9.0	23.8
34015	Sawed	5.5	20.0
34015	Planed	11.2	20.8
34116	Sawed*	8.4	22.7
34116	Planed	11.8	24.0

*Saws were sharpened immediately before the preparation of Sample No. 34116.

These results are somewhat surprising as ordinarily there would be obtained a higher percentage of soluble solids when the moisture content is lowered. The indications here, however, are that under certain conditions marked changes in the composition of the leather take place during its preparation. Since the moisture is greatly reduced by sawing it seems natural to conclude that this change in the leather is brought about by overheating. In fact during the sawing of the samples a slight heating-up was noticed, which it was realized would somewhat affect the mois-

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ture content, but it was not thought to be sufficient to otherwise alter the composition of the leather.

In view of these facts experiments were made to determine the effect on the composition of the leather of a moderate heat such as leather is subjected to in determining moisture. Two leathers were heated for 6 hours at 98°-100°C. and then exposed to the air for 18 hours. On analysis they gave practically the same percentage of soluble solids as the corresponding unheated portions.

TABLE II.

L. & P. No.	Treatment	Moisture per cent.	Soluble solids, moisture-free basis per cent.
34544	Unheated	8.9	28.1
34544	Heated	7.8	27.4
34545	Unheated	9.0	28.8
34545	Heated	7.7	29.2

Since these results show no effect on the water soluble content the indications are that the heating-up of the leather with certain machines is momentarily much greater than is generally realized. In this connection it would be interesting to go more thoroughly into this phase of the subject and to determine the maximum temperature to which leather could be heated without materially affecting the water soluble content. It is regretted that the pressure of other work has prevented doing this.

These experiments were carried out on finely shredded leather prepared by the modified machine which is described further on. In the preparation of these samples practically no change took place in their moisture content.

Knowing that several laboratories were equipped with circular saw machines, requests were sent out for descriptions of these machines and also for samples prepared by planing and sawing alternate strips from a block of leather, giving in this way a planed and sawed sample of leather as nearly identical as possible except for the method of preparation. Samples were received from three of these laboratories and the results obtained on them are given in Table III.

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TABLE III.

L. & P. No.	Preparation	Moisture per cent.	Soluble solids per cent.	Remarks
34110	Sawed in laboratory A	12.0	21.55	Exposed to air 15 minutes.
34110	Planed in laboratory A	12.2	22.40	Exposed to air 60 minutes.
34112	Sawed in laboratory B	8.9	16.50	Exposed to air 5 hours.
34112	Planed in laboratory B	9.9	17.40	Exposed to air 5 hours.
34114	Sawed in laboratory C	10.9	27.70	Exposed to air 30 minutes.
34114	Planed in laboratory C	11.7	27.60*	Exposed to air 30 minutes.

*Very coarse and thick shavings.

It will be noticed that the agreement here is decidedly better than in Table I though here too, even under the conditions of exposure of the prepared samples there is the tendency to lower moisture and soluble solids in the sawed samples. It will probably be interesting to point out, as well as it is possible to do so from information obtained through correspondence, how these machines differ from the one in this laboratory, which is composed essentially of four 8-inch saws each 1/16-inch thick and having a very slight set. The saws are of the cut-off type with rather small teeth, between three and four to the inch, and are driven by a ¼ horse-power motor. The speed of the machine originally was about 1,100 revolutions per minute when sawing, but this was increased immediately before the preparation of sample No. 34116 to about 1,500 revolutions per minute. The approximate speed when sawing is given as there is some slowing down from the speed when running free, probably because of the low power motor and also some slipping of the belt.

The machine in laboratory A has four 10-inch saws each 1/16-inch thick. They are of the splitting-saw type with large teeth, about one to the inch, and are driven by a ½ horse-power motor at about 1,500 revolutions per minute.

Laboratory B has a machine made up of four 8-inch saws each 1/16-inch thick and without set. The teeth are of medium size,

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two and two-thirds to the inch. The saws are driven by a 1 horsepower motor at about 700 revolutions per minute. Definite information concerning the type of saws has not been obtained but from a rough drawing they appear to be splitting saws.

The machine in laboratory C has three 8-inch saws each 1/16-inch thick with a slight set. The saws are of the splitting-saw type, with medium sized teeth, slightly less than two to the inch. The speed of the machine is 3,100 revolutions per minute.

In all of the machines the saw teeth are staggered.

It need hardly be stated that there is very little similarity between the essential features of the machines, such as the size and shape of the saw teeth and the speed at which the saws are driven. Because of this it is difficult to determine just what the controlling factors are in a machine which gives the best results. It will be noticed, however, that the last three machines have larger saw teeth than the one in this laboratory and also that at least two of these machines have "splitting" or "rip" saws instead of "cut-off" saws. No such general statement can be made concerning the speed. The indications are, therefore, that the size and type of saw teeth are the most important factors in preparing samples.

From the preliminary results given in Table III, especially concerning the moisture percentages, it was decided to secure several more samples prepared in laboratory A. A set of six samples, three planed and three sawed, gave the following results:

TABLE IV.*

L. & P. No.	Preparation	Moisture per cent.	Soluble solids per cent.
34316	Sawed	11.2	25.3
34316	Planed	11.5	25.1
34318	Sawed	11.1	24.0
34318	Planed	11.1	23.5
34320	Sawed	10.7	26.6
34320	Planed	10.6	26.5

*The above samples were bottled immediately after they were prepared.

The time of preparation for each sawed sample being about 15 minutes and for each planed sample about one hour.

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The agreement between the sawed and planed samples is excellent and it was decided, in view of these results, to modify the machine in this laboratory so that it would agree in general with that of laboratory A.

The old saws were replaced by four 10-inch ones each 1/16-inch thick, of the splitting-saw type, and having large teeth, about one to the inch. The saws have a very slight set and are driven by a 2 horse-power motor at approximately 1,500 revolutions per minute. Results on samples prepared by this machine together with those on duplicate samples prepared by planing are given in Table V.

TABLE V.*

L. & P. No.	Preparation	Moisture per cent.	Soluble solids per cent.	Fats per cent.
34526	Sawed	9.2	27.9	2.9
34526	Planed	9.7	27.1	2.7
34527	Sawed	8.9	24.1	3.4
34527	Planed	9.7	23.2	3.3
34528	Sawed	8.9	25.3	1.9
34528	Planed	9.3	24.1	2.0
34529	Sawed	7.8	28.7	3.1
34529	Planed	8.5	27.2	3.2
34530	Sawed	8.4	26.7	2.4
34530	Planed	8.9	25.7	2.2
34586	Sawed	11.9	19.4	2.4
34586	Planed	12.4	17.3	2.7
34590	Sawed	11.4	26.4	2.3
34590	Planed	11.3	24.7	2.4
34591	Sawed	10.9	27.5	1.2
34591	Planed	10.8	27.6	1.3

*All samples were bottled immediately after preparation.

The time of preparation for a sawed sample was about 15 minutes and for a planed sample about 45 minutes. The last three leathers were taken out of a humidity room maintained at 65°F. and 70 per cent. relative humidity, about 2 hours before their preparation.

These results show a decided improvement over those obtained by the old machine (Table I). The cutting action of the saws was much better and only a barely perceptible heating-up was noticed, in fact, no more than has been observed at times in planing a sample. The larger saws, however, create a strong

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draught which blows a great deal of the leather dust out of the machine. This is not only a nuisance but is also a menace to the operator. It may be possible to prevent this scattering of dust by a properly designed collection chamber although attempts to accomplish this have not yet proved successful.

It will be noticed that the moisture content of the sawed sample is generally slightly lower than that of the corresponding planed sample, the difference, however, is not great. As regards soluble solids, figures are now reversed. The sawed samples giving in every case, but one, decidedly higher percentages than can be accounted for by the slightly lower moisture content. This increase in the percentage of soluble solids could easily be explained as the result of the much finer division of the sawed samples, if it were not for the results previously given on samples prepared in laboratory A, which samples it will be noticed gave almost identical figures on both moisture and soluble solids. No satisfactory explanation can as yet be offered for the difference between the results given in Tables IV and V. The samples prepared with the machine of the Leather and Paper Laboratory appear to be more finely divided and somewhat freer from hard lumps than those prepared in laboratory A. This may account for the somewhat higher soluble solids recorded in Table V. There has been no opportunity, however, to secure more data, especially along the line of preparing the same leather with both machines.

It is possible that the loss of leather dust from the strong draught, to which reference has previously been made, is greater in the case of this laboratory's machine, and that possibly a concentration of the heavier particles of leather containing more water soluble matter takes place.

The results presented in this paper are of a preliminary nature, but since it is not possible to go more thoroughly into the subject in time for the annual meeting of the Association, it has been deemed advisable to give those so far obtained, with the hope that they will be of some value in a discussion of the subject.

There is need, however, for further study on samples of the same leathers prepared with several different machines, using as a basis for comparison a carefully planed sample of each leather.

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The importance of the proper preparation of leather samples and the need of a standard procedure cannot be too strongly emphasized, especially at this time when leathers are being so largely bought on specifications covering composition.

LEATHER AND PAPER LABORATORY,
Bureau of Chemistry,
Department of Agriculture,
Washington, D. C.

PROBLEMS FOR THE CONSIDERATION OF THE AMERICAN LEATHER RESEARCH LABORATORY.*

By F. H. Small.

The words "Research Laboratory" have proved an "Open sesame" to the pocketbooks of the tanners; but the magic has been in the delightful vagueness of the picture they conjured rather than in a clean-cut outlining of definite end to be attained.

The control and direction of the laboratory is in the hands of a capable and competent committee made up of members from both the National Association of Tanners and the American Leather Chemists' Association. This Committee can be trusted to see that the laboratory is put to the best possible use. Until such time, however, as the laboratory is started on a definite program, it is to be presumed that the Committee will be glad to entertain suggestions as to desirable lines of work that may be undertaken by the chemist in charge, and the following is presented in the hope that it may support the claim for consideration of a certain type of research, rather than of some particular problem or problems.

If we consider the various ideas we hear mentioned of what a research laboratory should be or do, we find that they group themselves pretty generally into three classes, which we may call the commercial class, the practical class, and the idealist class.

The exponents of the commercial class suggest that the research laboratory should do sampling, make analyses, adjust analytical disputes, determine whether merchandise is up to specification; in short, should serve as a combination trade laboratory and court of arbitration. While it is conceivable that a labora-

*Read at the Atlantic City meeting of the A. L. C. A., May 17, 1918.

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tory established for such purpose might serve a useful end, such a laboratory could not be called with any accuracy a "Research Laboratory." It would be a profound pity for the laboratory to concern itself with such routine or trade matters, when there is a real need in connection with our industry for "diligent, protracted investigation especially for the purpose of adding to human knowledge," as the dictionary defines "Research." It is sincerely to be hoped that the laboratory may not be diverted from the purpose implied in its name. There certainly is no lack of subjects for study and of pressing importance, and no time can afford to be wasted in merely commercial work for the handling of which ample facilities exist in the various trade laboratories.

The exponents of the practical class call for the study of problems of direct, immediate bearing on leather production, with the intent that what knowledge is gained may be promptly turned into dollars and cents and repay initial investment. The shortest method which will secure the required knowledge is, therefore, the most desirable, the primary idea being to get the answer regardless of whether one knows why it happens to be the answer.

The exponents of the idealist class would like to see the research laboratory devote itself to a study of fundamentals,—of the underlying laws governing the intricate phenomena attending the conversion of hide into leather. For them, the problem attacked would matter little and the results attained, regarded from the point of view of immediate expression in terms of dollars and cents, be a matter of comparative indifference. The real test would be, whether a step had been taken toward the day when, any given set of conditions having been formulated, the event may be predicted; that is, the day when leather-making has become an exact science.

To illustrate by an example, let us consider the swelling of hide in acid solutions. For the one we have called the Practicalist, the problem defines itself as a determination of the factors which affect the swelling,—a knowledge to be gained probably by the cut-and-try method. When the various acids are listed in the order of the degree of plumping they produce, and the effect of concentration, temperature, etc., is found, the problem is considered solved. For the Idealist, however, the actual experi-

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mental work may be the same as that of the practicalist but the underlying thought for him is,—What is it that makes hides swell? What are the fundamental causes? Are these capable of expression in any general law? He would not consider the problem solved until he had found such a law. When he had found it, he would have in his hands an answer to any question pertinent to the subject; no more cutting-and-trying would be needed: the effect resulting from any set of conditions covered by the law would be predicable. Of such character as this latter was the investigation carried on by Professor Procter and his assistants, on the swelling of gelatin in acid solution.

I would not argue for a moment that the sole purpose of the laboratory should be the consideration of hypothetical questions of remote practical interest, nor that such useful information as may be gathered by the way should be neglected. Professor Procter's researches on the acid-swelling of gelatin extended over a period of some 20 years,—though during this time he was doing much other work of immediate practical bearing,—and it may well be doubted whether the patience of our tanner friends would hold out for 20 years if no visible, tangible results were apparent as a result of the work of the laboratory before the end of such period. It is by no means necessary that the distinction between the practical and the idealist classes should be absolute. Overlapping certainly is permissible, probably desirable; but there is no doubt in my own mind that the thought back of every research, should be the co-ordination of the specific problem with our present knowledge of basic laws and the use of experimental information gained, to amplify this knowledge. This does not necessarily mean that one must determine the origin of the life germ before one can make a start in studying the tanning process even though such a course was thought desirable by a man who had a tanning machine to sell and who began the story of the virtues of the machine as follows:

"In reference to civil engineering chemistry which is now applied in the leather industry, I will cite some facts later and prefer to reach back to the elementary Patachneological conditions of the structure of an animal hide as a base of my object. I will explain to you that the physiology of a skin already starts in the creative embria. This of course is a archeotype process reaching

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far back to the Miocean and Geocean Periods, scientist are eager to link the existence of the embria and huf animal life to the Palaeozoic periods. This of course would mean hundred of millions of years since the production of animal industry started. For an example: We have traces that the Souriers, the Dinousiers, the Mastodon, even the pedigree of the flying animals covered with hair and scale called the Majos Chopa, are all of the same outcome. * * *

* * * * * * * * * * *

"A skin or a hide is composed of the epidermis, malpighi, *recte malpighi*, the corein layers perforated as they are, the blood corpuscles passing in for the respiration and the maintenance of the temperature and assimilation of food. If I have shortly outlined of what a hide or skin is consisting, it is done more to make a short story of these complicated material and now I am to refer how marketable leather has been produced since the Mediaeval time and how the leather industry has benefitted by the applying of up-to-date engineering chemistry."

While I do not advocate delving into the mysteries of prehistoric ages in the above fashion in the hunt for basic principles, I do wish to insist that the underlying thought of all research should be to get at fundamental causes and laws. If it is true that the largest field of usefulness of the laboratory may be found in a combination of the ideas of the practical and idealist classes, then the search for fundamental laws well may be sought through research on practical tannery problems,—and so long as one is keenly studying phenomena, adding diligently to our store of available knowledge it should not be held against him that the information gained is not always the exact information sought. Certain problems will seem to stand apart, to have no related interests; but it will be difficult to carry through any investigation without securing some new knowledge, some different viewpoint, which perhaps will help in some other research. W. R. Whitney has written (The Annals of the American Academy of Political Science, May, 1915):

"We can never quite appreciate the incredible applicability and utility of new facts of nature. We are repeatedly shown by our experience; but each new example only augments our stock of wonderment, of bewilderment. A very few months ago a certain

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well-known scientific investigator (Lord Raleigh) found a slight difference in the density of nitrogen taken from air and nitrogen derived from other sources. He felt obliged to know about this little difference. In co-operation with Sir William Ramsay he discovered argon. This was present in the atmospheric nitrogen and had always escaped detection. It formed less than 1 per cent. of the air. It was discovered to be entirely inert and chemically inactive. This was an apparent promise of great chemical uselessness.

"At that time it was exceedingly difficult to separate it from the air, and except for its scientific interest it seemed destined to be left inactive. Newly discovered methods of liquifying air and of combining nitrogen for fertilizer, as in the cyanamid process, have just made the argon available commercially. Other purely scientific research had shown the value of such a gas in incandescent lamps, and it is just at this time being used to produce the most efficient incandescent lamps of our knowledge. It was the recently discovered difference between this gas and other gases which made this lamp possible. When its existence and properties were known, its application was relatively simple and easy."

If, therefore, the research laboratory is slow in reaching an answer to some problem which seems of pressing importance, it yet may be doing valiant service for our cause, and as one who knows from experience the difficulties attendant upon research, I would bespeak for the laboratory an abounding patience from its founders.

There is yet one more thought I wish to advance before trying through discussion of a few definite problems which have been or may be suggested for the consideration of the research laboratory to illustrate my viewpoint. A letter received from Mr. J. A. Wilson reads:—

"From the soak vats to the finishing-room we are dealing with physical chemistry and the colloidal state to such an extent that I believe real progress (barring accidental discoveries) can be made only by scientists of the very highest order. Professor Procter fully realized this when he undertook the study of the acid-gelatin equilibrium over 20 years ago. When the principles underlying each process have been thoroughly mastered, then we may expect progress of a healthy nature."

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The result of Professor Procter's research on the acid swelling of gelatin is embodied largely in the formula:

$$e = -2x + 1\sqrt{4x^2 + z^2},$$

a rather unpromising-looking conglomerate to hand your yard-foreman by which to regulate the plumping of his hides. As a matter of fact, it will tax the ability of many of us chemists to dig out the information locked up in those x's and z's. Many of the fundamental laws relating to our industry are not susceptible of simple expression and we are going to need not only competent research chemists but as well competent interpretative chemists, who can take the proven laws and demonstrate the possibilities of scientific leather-making on the basis of these laws.

You may wonder that I have used the same example, *viz.*, Procter's work on the acid-gelatin equilibrium, several times to illustrate my thought, but the sad fact is that in our special branch of chemistry the research of Professor Procter and his associates is practically the only instance we have of whole-hearted attempt to get at fundamental laws. There seems all the more need, therefore, that our research laboratory should do its bit to keep the above work from being lonesome.

Turning now to some of the possible and suggested topics for investigation,—the curing and disinfection of hides has been mentioned. This primarily is of interest to the Government through its Bureau of Animal Industry, which aims to take preventative measures against contagious animal diseases, and among others, against such as are capable of propagation through hide-contained germs. In a sense, a suitable method of disinfection is their hunt, and any method having their approval must needs be efficient in disinfecting the hide. The interest of the tanner begins when he has this disinfected hide to tan, and what concerns him is, whether this disinfecting process has affected yield or quality of leather. It may be that the modern tanner has reached that state of trustfulness when he will accept a finding from a laboratory on this point; but it is my private opinion that if outwardly he has, he yet will steal in the back way and have a look at his leather and watch the Lot figures before he will be thoroughly content.

Then there is the question of the disposal of tannery waste,

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utilization of sludge, etc. This is bound to be affected largely by local conditions, and so not prove capable of general solution. It is really more of an engineering than a chemical problem, and is probably susceptible of adequate test only on a large scale of operation. It does not analyze out as a very satisfactory subject for investigation in a leather research laboratory. There is one tannery-waste problem, however, that may be worthy of attention by the research laboratory at this time and that is the working out of a practical method for the recovery of the chrome in waste chrome liquors. I believe this rather a problem for the tannery laboratory than the research laboratory, and that with a complete knowledge of the laws underlying chrome tannage it probably will be possible to utilize chrome liquors completely, so leaving no problem; but just at present the problem of the utilization of every bit of chrome on hand is so vital that it must be regarded from quite another aspect than what it would be were these normal times.

Another suggested subject is, Shoe-Leather Quality; the Value of Chrome Re-tan vs. Vegetable Tan; the Effect of Sugar and Salts on Wear, Water Penetration, etc. This really is rather a trade topic and there is already one research of the sort under way at Mellon Institute, another at the leather and paper laboratory, another at the Bureau of Standards, and possibly others in private laboratories. Is it desirable to add to the number?

Then there is a suggestion that a study be made of Methods for Determining Free Mineral Acids in Leather. This is a matter of such immediate and direct practical importance to the tanners that it well may come in the list of subjects that will more or less of necessity be studied in the laboratories of the tanners. It has been and is now under study by a Committee of the American Leather Chemists' Association. Is it the sort of thing to which the energies of the research laboratory should be devoted? Personally, I have grave doubts whether the research laboratory would be fulfilling its purpose in the largest way if it devoted its energies to the study of analytical methods as an end in itself. Such study may be necessary as part of a larger problem, but *per se*, it seems questionably desirable. There is a subject closely related to acid determination which would seem to be rather more plausibly suitable for study, and that is, whether

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the use of sulphonated oils in leather is wise; whether they do not break down with the liberation of free sulphuric acid, and consequent damage to the leather. Study of this subject might necessitate study of a method for the determination of free sulphuric acid in leather.

This Spring, there has been on the market a relatively large amount of undertanned leather, leather having a so-called raw streak. The onus for this condition has been put on the shoulders of the Fuel Administration and the weather man, and the trouble has been ascribed to cold liquors. Is it true that the rate at which tanning proceeds is dependent on temperature? If so, does any law govern? Can we tell the tanner how much longer it will take him to tan his leather if his liquors are at 50° F. than at 70° F.? Here is a subject that seems to have large possibilities, to open up most delightful fields of research and research which well may have to do with fundamentals. Surely other things besides temperature affect rate of tanning. In order to study temperature effect we must know what these others are. Is there a rate of tanning characteristic of each material? Will quebracho tan at a certain definite rate, and oak at another? Is this rate characteristic of quebracho tannin and of oak tannin and if so, are the differences measurable and can the measurement of the rate be used as a means of identification of the tannins from different materials? Or again, is the rate dependent on the so-called non-tannins which accompany the tannin in any given material? Here we perhaps shall be able to throw some light on the moot question of the value of high *versus* low non-tannins in the making of leather. How does a chestnut extract with high non-tannin differ from one with low non-tannin in its effect on the making of leather,—assuming that the raw material is the same in each case and the resultant differences are due to different methods of leaching? This brings up the question of the conditions of leaching which give maximum yield, and whether maximum yield is compatible with greatest suitability for making leather. In this latter connection will come up the question of the nature of the non-tannins, when high and low, so that we may know how they will behave under manufacturing conditions in the tan-yard, whether they will develop acid, etc. And we may ask in passing, Can the production of acid in the

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tan-yard be controlled? Can desirable acids be produced to the exclusion of undesirable acids, or moulds?

But so far we have assumed that the rate of tanning depends only on the tanning material, and we know that it is equally dependent on the condition of the hide. This opens up the question of handling hides in the beamhouse,—the place where the tanner tells us the quality of his leather is made, and the place which probably is the least under any sort of scientific control of any department of the tannery. The beamhouse processes all need elucidation. What is the best method of soaking green-salted or dry hides and why is it the best? What is the effect of using water at different temperatures,—of using chemicals,—of not removing the salt? Why do we get different results when we use lime from those obtained when we use sulphide, or when we use a mixture of the two? If we use a mixture, how should it be made: by adding the sulphide to the lime while slaking, or by adding the dissolved sulphide to the milk of lime? Does this make any difference and, if so, why? What is the effect of varying temperature,—of age,—of the presence of hide-decomposition products? Should the hide be bated or acid-drenched, or neither? What difference in the hide structure is caused by these different factors and how do they affect rate of penetration of tannin, leather yield and leather quality? It is almost immaterial with what specific problem one starts, the whole field is open, and definite information about fundamental causes which will lead to an intelligent regulation of beamhouse procedure under laboratory control is sadly needed.

I have propounded most of the above suggestions as relating more particularly to vegetable tanning; but it is probable that an attempt at securing data, working out fundamental formulas, etc., might better begin with the chrome process, where one at least of the components, *viz.*, the tanning material, is not so complex.

In any research on questions like the above, utilization of all the growing knowledge of physical and colloid chemistry will be a necessity; but such utilization will certainly result in a saving of time, if not a saving of mental effort. The paper by Wilson and Kern on the action of neutral salts upon chrome liquors seems an admirable illustration of what is possible, and

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the reasoning, based on the researches of Procter, by which Coombs and McGlynn in their article on "Tanning in Acid Liquors" in the March 15th issue of the *Journal of the Society of Chemical Industry*[3] for 1918, explain the causation of a black streak in the heart of their experimental leather is extremely interesting, especially since the reasoning led to a removal of the trouble.

In the letter above referred to from J. A. Wilson, he writes: "As for the new Research Laboratory, I would suggest that the chemist in charge be given a free hand to do such work as he may see fit to bring out the fundamental principles underlying each of the processes employed in making leather. The task may seem enormous, but a good chemist, having nothing else to worry him, should be able to make sufficient headway to make the undertaking worth while. Such work may be branded with the much abused term "theoretical," but in my opinion it is immensely practical." Time and a process of education may be needed to make the last sentence believable; but I am in hearty accord with Wilson in his statement, and I sincerely hope that, whatever, the work undertaken by the research laboratory, it may have as its underlying thought, to get as close to basic causes and basic laws as is humanly possible.

THE ACTION OF NEUTRAL SALTS UPON CHROME LIQUORS.

Arthur W. Thomas, Ph. D. and Mabel E. Baldwin, M. A.

A study of the influence of neutral salts upon chrome liquors by the electrometric method has revealed some very surprising facts. It has indicated the existence of factors in the reaction of chrome liquors which were previously unknown, and shows that a knowledge of these factors is essential to a proper understanding of the mechanism of chrome tanning.

Some previous work on the action of neutral salts upon chrome liquors has been reported by Wilson and Kern.[1] Following the ideas set forth in their paper the general plan of this work has been, first to make a more detailed study of the influence of time upon the hydrogen ion concentration of chrome liquors, some results on which have already been given in an earlier paper.[2]

[1] This JOURNAL, 12, 445 (1917).
[2] This JOURNAL, 13, 192 (1918).
[3] This JOURNAL, 13, 255 (1918).

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TABLE I.—Influence of Time Upon the Hydrogen Ion Concentration of a Chrome Liquor After Addition of Sodium Chloride and Dilution.

Time hrs.	min.	Log. C_H + *	Conc. hydrogen ion moles per liter
	10	3.00	0.00100
	20	2.94	0.00115
	30	2.89	0.00129
	40	2.85	0.00141
	50	2.82	0.00151
1	00	2.79	0.00162
1	10	2.77	0.00170
1	20	2.75	0.00178
1	30	2.73	0.00186
1	40	2.72	0.00191
1	50	2.70	0.00200
2	00	2.70	0.00200
2	10	2.69	0.00204
2	20	2.69	0.00204
2	30	2.68	0.00209
2	40	2.67	0.00214
2	50	2.66	0.00219
3	00	2.66	0.00219
3	10	2.66	0.00219
3	20	2.66	0.00219
3	30	2.66	0.00219
3	40	2.66	0.00219
3	50	2.66	0.00219
4	00	2.66	0.00219
4	10	2.66	0.00219
4	30	2.66	0.00219
4	50	2.67	0.00214
7	00	2.72	0.00191
9	20	2.75	0.00178
18	20	2.86	0.00138
20	00	2.87	0.00135
23	20	2.90	0.00126
25	00	2.90	0.00126
28	40	2.91	0.00123
34	00	2.92	0.00120
46	00	2.96	0.00110
52	10	2.96	0.00110
57	40	2.96	0.00110
3 days		2.96	0.00110
15 days		2.96	0.00110

*Log. C_H + means the logarithm of the concentration of hydrogen ion.

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and then to determine the influence of the presence of neutral salts upon the hydrogen ion concentration of the liquors.

In Table I are figures showing the progress of the change in "actual acidity" (exact concentration of hydrogen ion) taking place during the time required to reach equilibrium in a chrome liquor after the addition of sodium chloride and dilution. The liquor was made by adding 5.846 grams of NaCl to 3 cc. of the stock chrome liquor, then bringing the volume up to 50 cc. by adding water, the final concentration of Cr_2O_3 being 13.86 grams per liter and NaCl, 2 molar. Determinations of the hydrogen ion concentration were made every 10 minutes for 4 hours and then at longer intervals for 3 days. From the curve, Fig. 1, it may be

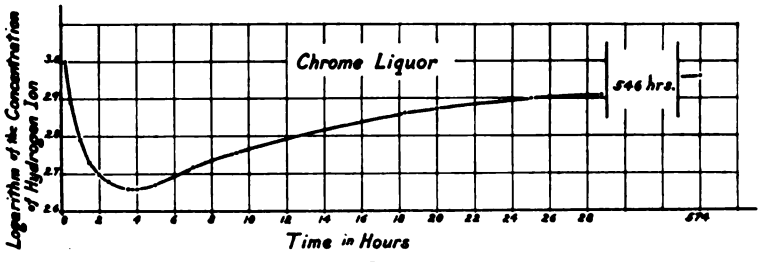

FIG. 1.

seen that, during the first 3 hours the "actual acidity" of the solution increased, during the fourth hour it reached a maximum, and after that decreased at a much slower rate until after 3 days it reached equilibrium.

From these results it appears that there are two reactions taking place in the solution, one increasing the concentration of hydrogen ion, the other decreasing it, but with unequal velocities. It is, therefore, evident that equilibrium in a chrome liquor is not reached almost instantaneously as has been previously supposed, but that the time factor is an important one to be considered in the chemical control of the chrome tanning process.

The data given in Table II and Fig. 2, show the influence of neutral salts upon the actual concentration of hydrogen ion of chrome liquors. The salts used in this investigation were NaCl, NH_4Cl, Na_2SO_4, $MgSO_4$, and $(NH_4)_2SO_4$. Series of solution were made by adding to equal amounts of a stock chrome liquor increasing amounts of the different salts then water to a definite volume so that the resulting concentration of Cr_2O_3 was 13.86

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grams per liter and the concentrations of salt M/4, M/2, M, 2M, etc. In the case of NaCl the determinations of hydrogen ion concentrations were made immediately and again after the solutions had been standing for 15 days, while in the cases of the other salts the concentrations of hydrogen ion were determined only after 30 days.

The salts used were tested with indicators with the following results:

NaCl.....Neutral to azolitmun.
NH_4Cl.....Acid to azolitmun, neutral to methyl orange.
Na_2SO_4.....Neutral to azolitmun.
$MgSO_4$.....Neutral to azolitmun.
$(NH_4)_2SO_4$.....Acid to azolitmun, neutral to methyl orange.

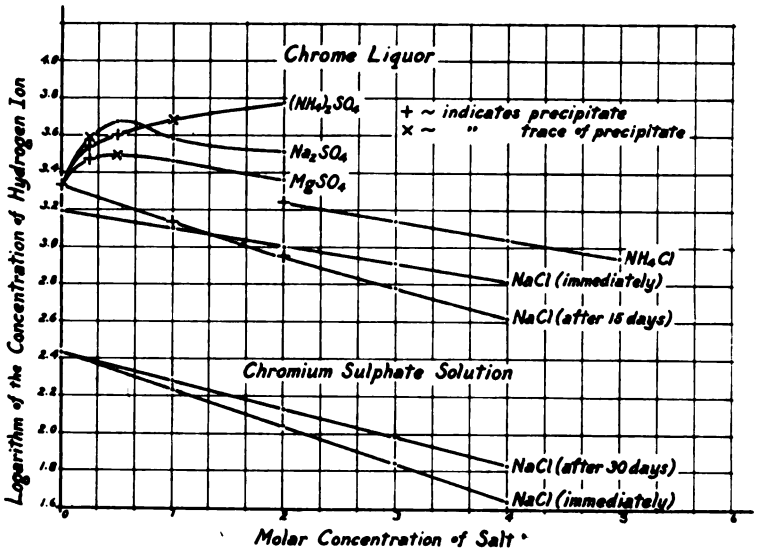

FIG. 2.

The stock chrome liquor, according to the analysis obtained from Mr. Wilson, showed:

Cr_2O_3.....14.3 % by weight.
Fe_2O_3..... 1.9 % by weight.
Al_2O_3..... 0.2 % by weight.
Total SO_3.....23.5 % by weight.
NaCl..... 0.4 % by weight.
Glucose.....None.
Specific gravity.... 1.628 at 80° F.
Basicity, corresponding to $Cr(OH)_{1.34}(SO_4)_{0.83}$

The influence of NaCl upon the hydrogen ion concentration of

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a pure chromium sulphate solution was also studies and the results are given in Table II and Fig. 2.

TABLE II.—Effect of Neutral Salts Upon the Concentration of Hydrogen Ion of Chrome Liquors.

CHROME LIQUOR.

Conc. salt	Log. C_H^+ immediately	Conc. hydrogen ion moles per liter	
	Sodium Chloride.		
O	3.19	0.00064	No precipitate
M	3.10	0.00079	No precipitate
2M	3.00	0.00100	No precipitate
3M	2.92	0.00151	No precipitate
4M	2.81	0.00195	No precipitate
Conc. salt	Log. C_H^+ after 15 days	Conc. hydrogen ion moles per liter	
	Sodium Chloride.		
O	3.33	0.00047	Precipitate
M	3.14	0.00072	Precipitate
2M	2.95	0.00112	Precipitate
3M	2.78	0.00166	No precipitate
4M	2.62	0.00240	No precipitate
Conc. salt	Log. C_H^+ after 30 days	Conc. hydrogen ion moles per liter	
	Ammonium Chloride.		
O	3.33	0.00047	Precipitate
2M	3.24	0.00057	Precipitate
3M	3.14	0.00072	No precipitate
4M	3.04	0.00091	No precipitate
5M	2.95	0.00112	No precipitate
	Sodium Sulphate.		
O	3.33	0.00047	Precipitate
M/4	3.59	0.00026	Trace of precipitate
M/2	3.67	0.00022	No precipitate
M	3.58	0.00026	No precipitate
2M	3.51	0.00031	No precipitate
	Magnesium Sulphate.		
O	3.33	0.00047	Precipitate
M/4	3.47	0.00034	Precipitate
M/2	3.49	0.00032	Trace of precipitate
M	3.46	0.00035	No precipitate
2M	3.36	0.00043	No precipitate
	Ammonium Sulphate.		
O	3.33	0.00047	Precipitate
M/4	3.54	0.00029	Precipitate
M/2	3.60	0.00025	Precipitate
M	3.68	0.00021	Trace of precipitate
2M	3.77	0.00017	No precipitate

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CHROMIUM SULPHATE SOLUTION.

SODIUM CHLORIDE.

Conc. salt	Log. CH. immediately	Conc. hydrogen ion moles per liter
O	2.43	0.00372
M	2.22	0.00603
2M	2.04	0.00912
3M	1.84	0.01446
4M	1.63	0.02344

SODIUM CHLORIDE.

Conc. salt	Log. CH. after 30 days	Conc. hydrogen ion moles per liter
O	2.43	0.00468
M	2.28	0.00525
2M	2.13	0.00741
3M	1.98	0.01047
4M	1.83	0.01479

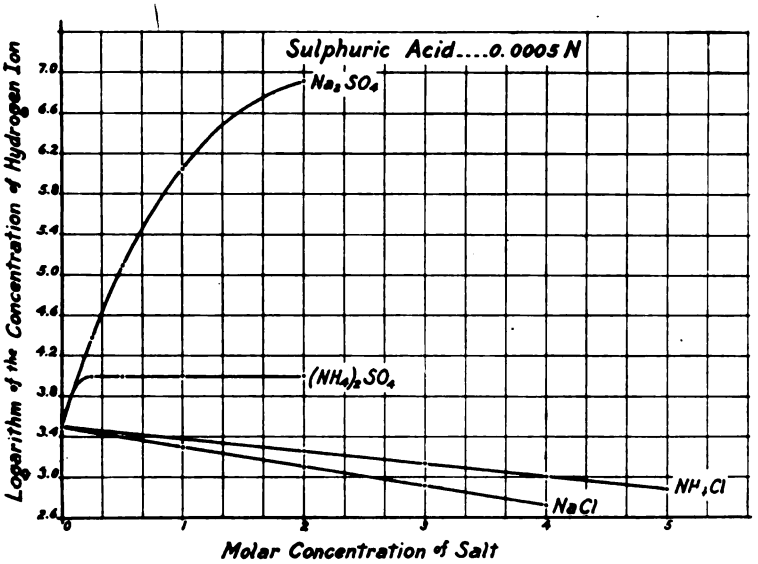

FIG. 3.

In Table III and Figure III are the figures from similar experiments in which the influence of NaCl, NH_4Cl, $(NH_4)_2SO_4$, and Na_2SO_4 upon a pure sulphuric acid solution was determined. The sulphuric acid used was 0.0005 N.

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TABLE III.—Effect of Neutral Salts Upon the Concentration of Hydrogen Ion of Sulphuric Acid, 0.0005 N.

Conc. salt	Log. C_H^+	Conc. hydrogen ion moles per liter
	Sodium Chloride.	
O	3.50	0.00032
M	3.29	0.00051
2M	3.10	0.00079
3M	2.92	0.00120
4M	2.71	0.00195
	Ammonium Chloride.	
O	3.50	0.00032
2M	3.27	0.00054
3M	3.14	0.00072
4M	3.00	0.00100
5M	2.88	0.00132
	Ammonium Sulphate.	
O	3.50	0.00032
M/4	4.00	0.00010
M/2	4.00	0.00010
M	4.00	0.00010
2M	4.00	0.00010
	Sodium Sulphate.	
O	3.50	0.00032
M/4	4.37	0.00004
M/2	5.10	0.000008
M	6.05	0.0000009
2M	6.92	0.00000012

In all three cases, namely those of stock chrome liquor, chromium sulphate solution, and sulphuric acid, the influence of the presence of NaCl and NH_4Cl was to increase the concentration of hydrogen ion, although the amount of total acid hydrogen remained unaltered. Moreover, the increase in the concentration of hydrogen ion was in direct proportion to the quantity of NaCl or NH_4Cl added. This property of NaCl has been recorded before[3] although no satisfactory explanation has yet been advanced.

The effect of the presence of Na_2SO_4 and $(NH_4)_2SO_4$ upon sulphuric acid solution is in agreement with the law of molecular concentrations according to which the increased concentration of

[3] Fales and Nelson. "The Effect of Sodium Chloride upon the Action of Invertase." *Jour. Am. Chem. Soc.*, 37, 2769 (1915).

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sulphate ion favored the union of the hydrogen ion and sulphate ion, thus diminishing the concentration of hydrogen ion.

In the case of chrome liquors, however, the influence of the presence of sulphate is much more complicated.

As recorded in the tables precipitates settled out from some of these solutions. The chrome liquor upon dilution with pure water gave a precipitate in less than 24 hours, but when a neutral salt was added the formation of a precipitate required a much longer time and in some cases was not complete even after 30 days. The presence of neutral salts therefore, retards the formation of a precipitate and the larger the amount of salt the longer the time required for the appearance of the precipitate.

Upon comparison of the hydrogen ion concentrations in the range of precipitation it becomes evident that there is no definite concentration of hydrogen ion at which precipitation begins.

In the light of these discoveries it is easy to expect that further research will result in such improvement of the processes of chrome tanning as to be of lasting benefit to the industry as a whole.

We are indebted to A. F. Gallun & Sons Company, of Milwaukee, for their generous support of this research and to Mr. John Arthur Wilson for his helpful suggestions.

LABORATORY OF COLLOID CHEMISTRY,
Havemeyer Hall, Columbia University,
New York City, May, 1918.

TANNING IN ACID LIQUORS WITH COMPARATIVE TESTS.*

By F. A. Coombs and W. H. McGlynn.

These experiments were undertaken in the hope of throwing some light on the value of acid in tan liquors. The experimental process, as related to hide-sections for comparative results, has been described previously.[1] It will be noted that two experiments were made with acetic and one with sulphuric acid. Each experiment includes two tests and each test consists of two pairs suitable for comparative purposes. All the tan liquors were pre-

*J. S. C. I., March 15, 1918.

[1] J. S. C. I., Feb., 1917. This JOURNAL, May, 1917.

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pared from wattle bark and a normal and acid tannage was used for each experiment.

We have endeavored by a series of comparative tests to show the difference between the results obtained with normal wattle liquors and similar liquors with the addition of certain amounts of acetic acid. The hide sections were prepared for the tan-liquors in the way already described (*loc. cit.*). For the acid tannage in the first two experiments, the natural acidity of the wattle liquors was found by the lime-water test and was then made up to the required concentrations by addition of acetic acid. The difference between the acidity of the liquors in the normal and acid tannages will show the amount of acetic acid used for the latter.

The influence of acid on the quality of leather during the process of tanning varies to a considerable extent according to the acid used and its concentration at various stages. Generally it may be said that tanners use acid to plump or swell the hide, thereby obtaining a stouter and consequently a more valuable leather. Our problem was one of determining its influence on the quality of heavy leather.

Our experience teaches us that all skins in the pelt state respond quickly to the plumping action of dilute solutions of various acids, but they do not respond to this action after they have been tanned. Sheep pelts are tanned in weak solutions and fix the minimum amount of tannin, but the resulting leather successfully resists the plumping action of acids. A neutral pelt is soft and flabby, differing from the acid pelt, which is firmer and stouter. The physical difference between the acid and neutral pelt will be responsible for a difference between the qualities of their respective leathers, providing they are fixed in the condition described above and that tannin is the fixing agent.

It is generally recognized that a firm and stout leather is a desirable result in the production of sole leather and, therefore, within certain limits the best results from a monetary standpoint will be obtained by fixing the pelt in the acid condition. A soft, pliable leather will be the result when a neutral pelt is tanned in liquors containing the minimum amount of acid; but when a highly plumped acid pelt is placed in acid liquors capable of keeping the pelt in its swollen condition, a harsh and brittle leather is

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produced, which, in extreme cases, will break like a biscuit. The wear by friction will always be greater on a brittle than on a pliable leather and the most prominent factor in this physical difference appears to be one of elasticity.

ACETIC ACID EXPERIMENT. No. 1.

FIRST TEST.

	Sections 2 and 5. Normal wattle bark liquors.		Sections 1 and 6. Acid wattle bark liquors.	
Days	Barkometer	Lime-water	Barkometer	Lime-water
3	8°	2.3	8°	10
5	12°	2.8	12°	12
6	17°	3.1	17°	14
8	24°	5.1	24°	16
12	33°	7.2	33°	18
19	46°	9.5	46°	20
21	60°	9.9	60°	22

SECOND TEST.

	Sections 4 and 7. Normal wattle bark liquors.		Sections 3 and 8. Acid wattle bark liquors.	
Days	Barkometer	Lime-water	Barkometer	Lime-water
2	8°	3.1	8°	10
4	12°	4.3	12°	12
6	17°	5.3	17°	14
8	23°	7.1	23°	16
11	32°	9.0	32°	18
19	45°	7.7	45°	20
21	57°	9.0	57°	22

For the first experiment a pelt which had been declimed on the surface with lactic acid was used. This pelt was placed in the first tan liquor containing acetic acid and the tannin penetrated a certain distance into the hide, fixing a portion of the fibers and producing a normal leather. At this stage about one-fifth is tanned and the other four-fifths of the hide has fixed a certain amount of acid. As the pelt moves forward through the various tan-liquors their acidity is gradually increased and the amount of acid fixed by the untanned portion of the hide also increased until the tannin has penetrated through the hide. Under normal Australian conditions the tannin takes from 3 to 4 weeks to penetrate into the center of the hide and, therefore, all the plumping must be done before the end of the fourth week. The leather tanned in the acetic acid tan liquors (first experiment) had a dark streak of brittle fiber in the center of the

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hide and this brittle portion would represent that part which was not tanned after the leather had been in the tan liquors for 2 weeks. At this stage we apparently had an acid concentration capable of swelling the untanned portion of the hide beyond that point at which harsh leather is produced, providing it is fixed in this abnormal condition.

ACETIC ACID EXPERIMENT. No. 2.

FIRST TEST.

	Sections 2 and 5. Normal wattle bark liquors.		Sections 1 and 6. Acid wattle bark liquors.	
Days	Barkometer	Lime-water	Barkometer	Lime-water
2	8°	3.2	8°	6.0
4	12°	4.3	12°	8.0
6	17°	4.3	17°	10.0
9	23°	6.1	23°	12.0
13	32°	6.2	32°	18.0
21	45°	9.4	45°	20.0
22	58°	10.2	58°	22.0

SECOND TEST.

	Sections 4 and 7. Normal wattle bark liquors.		Sections 3 and 8. Acid wattle bark liquors.	
Days	Barkometer	Lime-water	Barkometer	Lime-water
2	8°	3.5	8°	6.0
4	12°	4.0	12°	8.0
6	17°	5.0	17°	10.0
9	23°	6.7	23°	12.0
12	32°	8.8	32°	18.0
21	45°	9.0	45°	20.0
22	58°	9.8	58°	22.0

In dilute acid solutions the protein molecules of the hide combine with the acid to form a highly ionizable salt, and under certain conditions the concentration of diffusible ions in the hide is greater than the ionic concentration in the outer solution, which leaves the osmotic forces in the two phases in an unbalanced state and, as a result, the external solution is absorbed and the hide begins to swell. These forces are described, by Procter and Wilson, for gelatin as an outward pull where the increase in volume is directly proportional to the pull. Now let the total elongation of the hide fibers due to any outward pull be represented by a straight line AB. If the soft flaccid neutral pelt be placed at A and the firm stout acid pelt at B, we will have a scale for the total elongation between the neutral pelt at zero

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and the acid pelt at the elastic limit. Suppose we now take a pelt swollen to 9° and place it in a tan liquor with the required acid concentration to keep it at that figure, then tannin would fix the pelt and give it a permanent set at 9° elongation.

When these sections were placed in tan-liquors the outer portions of the hide received a permanent set at a low figure, but as the leather was moved forward into liquors with higher acid concentrations, the figure for the permanent set would gradually increase. In this case it would appear as if the permanent set for the inner portion of the hide were too near the elastic limit for the production of good leather. Working on this theory we reduced the amount of acid during the early stages of the tanning process as shown in the second experiment, and the resulting leather was free from this fault, which was constant for all the acid leather from the first experiment.

Procter states that after the swelling has reached its definite value, it is unchanged at a constant temperature by further lapse of time, providing that no change takes place in the acid concentration of the outer solution. Thus the total elongation for a swollen pelt is directly related to this acid concentration, and if it is desirable to have a permanent set at any particular point on the scale for elongation, then the correct acid concentration must be maintained in the outer solution.

We also give results for leather swollen with sulphuric acid. The sections were treated in the usual manner before they reached the tanning process and then one-half was placed in a sulphuric acid solution for plumping purposes. It is not desirable to give a permanent set to the grain or superficial surface of the corium at a high elongation because this portion of the hide is the first to crack if the process tends to a brittle leather; therefore, it is the usual custom to allow the tannin to penetrate the grain of the normal hide and then place it in the sulphuric acid solution.

Several experiments were carried out with pelt suspended in acid solutions of varied concentrations, and we finally decided to use an N/10 sulphuric acid solution for the first test in this experiment. The pelt was placed in a tan liquor 8° barkometer for 2¼ hours, at the end of which time the grain was permanently set. The leather then went into N/10 and N/15 sulphuric acid solution for first and second tests respectively, and was left

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overnight for a period of 17 hours. The remaining tanning process was the same for these sections as for the normal process. The sections were very firm when they came from the sulphuric acid solution, and the increase in weight was 1 per cent. on the lime-swollen pelt. They did not receive any lactic acid. The penetration of the tannin proceeded less quickly with the sulphuric acid than with the normal leathers and while the acid process gave the stouter leather, or greater dimensions as represented by a straight line piercing the leather at right angles to the grain, it appeared to be the cause of a decrease in area. Thus any increase in this direction would not be directly proportional to the increase in volume.

SULPHURIC ACID EXPERIMENT.

FIRST TEST.

	Sections 2 and 5. Normal wattle bark liquors.		Sections 1 and 6. Acid wattle bark liquors.	
Days	Barkometer	Lime-water	Barkometer	Lime-water
1	8°	2.5	8°	2.5
3	12°	2.6	12°	2.6
5	17°	3.5	17°	3.5
8	23°	5.6	23°	5.6
17	32°	6.2	32°	6.2
21	45°	8.7	45°	8.7
26	60°	10.6	60°	10.6

SECOND TEST.

	Sections 4 and 7. Normal wattle bark liquors.		Sections 3 and 8. Acid wattle bark liquors.	
Days	Barkometer	Lime-water	Barkometer	Lime-water
1	8°	2.7	8°	2.7
4	12°	3.0	12°	3.0
5	17°	5.7	17°	5.7
9	23°	5.6	23°	5.6
17	32°	6.8	32°	6.8
19	45°	9.0	45°	9.0
23	60°	11.4	60°	11.4

When the partially tanned pelt was removed from the sulphuric acid solution and placed in the tan liquors no attempt was made to keep up the acid concentration in the outer solution. The unstable collagen—sulphuric acid combination is hydrolized and the acid diffuses into the outer solution, where a portion displaces weak acids from those salts common to tan liquors. Under these conditions most of the sulphuric acid is removed from the leather at the end of the tanning process. Any sulphuric acid process, to

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be efficient, should not leave free sulphuric acid in the dry leather. This acid is used in quantities varying from 20 to 50 pounds for 50 hides, and the pelt swells to a considerable extent; but before the whole of the hide is permanently set a large portion of the acid will have been removed by the various tan liquors. With the sulphuric acid process, the amount of acid fixed by the hide reaches its maximum at the beginning of the tanning process, and if the swollen fibers are exposed to the tannin solution by cutting a piece off the hide, the cut surface appears to fix a large amount of tannin, and changes to a deep red. If, however, the conditions are such that the untanned portions of the fiber are gradually giving up acid to the outer solution before they are fixed by the tannin, the resulting leather is not a dark red color providing sufficient acid diffuses out of the hide.

Procter and Wilson state that the rate of tanning will be a maximum for a given concentration of liquor when the potential differences are of opposite signs and the absolute value of each is a maximum. We have found, that after the second week, the acetic acid in the first experiment reached a certain concentration in the untanned portion of the pelt, and as a direct result an excess of tannin was fixed as indicated by the dark red streak in the center of the hide. Under certain conditions the same dark red color could be obtained with the sulphuric acid leather. To obtain these results the differences in potential must have reached its maximum for these experiments when the pelt had fixed the maximum amount of acid. As the difference in potential increases, the rate of penetration would appear to decrease, and it is probable that at a certain point, tannin is deposited on the fiber in sufficient quantities to form a barrier to further penetration.

We have seen sole leather with an untanned streak in the center of the dark red leather and this was supposed to be due to some abnormal state in the sulphuric acid process. As the tannin diffuses into the hide it will choose the paths of least resistance and diffuse along the less dense spaces between the fibers. These spaces probably contain a weak solution of protein matter which is precipitated by the tannin, leaving what are known as air spaces in the dry leather. When the hide fibers swell under the influence of acid solutions, the outward pull may be directly pro-

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portional to the increase in the volume of the individual fibers; but in swelling they will tend to fill up any open spaces in the hide and retard the penetration of the tannin. If there are open spaces in the hide at this stage the outward pull (for a hide) would not be directly proportional to its increased volume as measured by external dimensions.

The amount of tannin fixed by a hide is proportional to the concentration of tannin in the liquors. In the normal tanning process the pelt is first placed in weak liquors. This was probably rendered necessary in the past because the hides contained a considerable amount of lime when they reached the first tan-liquors, and calcium tannate would be precipitated on the outer portion of the leather, with a tendency to retard the penetration of the tannin if strong liquors were used. The amount of tannin and calcium tannate deposited would then be at the maximum.

Strong liquors on a neutral or slightly acid pelt are supposed to give this undesirable result, which would be intensified with the higher percentages of acid as used in these experiments. There are several reasons for using weak liquors in the early stages of the tanning process, but if there is any value in the theory that an excess of tannin deposited on the fibers will retard penetration to an appreciable extent, then strong tan-liquors should not be used to fix the highly swollen sulphuric acid pelt in the early stages. A sound definition of "strong liquors" for the various stages in the process of tanning is impossible without another series of comparative tests to deal with this factor. Many tanners, more especially those who use bark and do their own leaching, would certainly start their hides in stronger liquors providing the loss was not excessive when pumping away tail-end liquors.

Our results for these experiments show that the amount of fixed tannin (see degree of tannage) increases with the acid processes, and from our water absorption tests we find that, as further amounts of tannin are fixed on the leather, greater resistance is offered to the penetration of water. The wear-resistance of leather will be proportional to the mass, other factors being equal, and as fixed tannin increases the mass this power of resistance will be proportional to the fixed tannin. If the

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combination between hide substance and tannin be a chemical one, then this portion of the leather is held together by cohesive forces, differing from the total solubles which are held in the leather by adhesive forces.

Both combined tannins in excess and water-solubles are capable of adversely affecting the results by imparting to the leather brittle qualities which will vary according to the tannins used. In a hot, dry climate leather containing large amounts of fixed tannins is inclined to become brittle or it loses some of its elastic properties. The same leather might give general satisfaction in Europe, where it retains that amount of water which is required to keep it in a pliable state. As far as sole leather is concerned, any brittle qualities which can be traced to any excess of combined tannins will not adversely affect the wearing qualities, providing the leather contains sufficient fatty matter and water.

The water-soluble matter in leather is brittle or plastic according to the amount of water it contains, and therefore, varies with atmospheric changes, tending to a harsh, brittle leather in a dry climate and offering very little resistance to the penetration of water. Owing to its hygroscopic properties glucose is useful for keeping a leather mellow or pliable during exposure to a high temperature and low humidity, but these properties render it extremely unsuitable in any climate for sole leather which must, at certain times, resist the penetration of water to a degree not attainable with a leather containing glucose. Fatty matters make leather pliable and enable it to offer great resistance to the penetration of water. Fats, but not glucose, are the necessary constituents of a good sole leather.

Riethof[2] states that sole leathers for the British and United States Governments are allowed to contain 25-26 per cent. of water-soluble matter. Temperature for extraction is not given. As both these Governments are advised by experts we assume that trained leather trade chemists are satisfied that this soluble matter contributes to a considerable extent to the wear resistance properties of sole leather. Water-solubles certainly increase the mass and may contribute to this desirable result mentioned above when they contain sufficient water to make them as plastic as cobblers' wax. There is very little evidence for and a good deal

[2] Hide and Leather, Jan. 5, 1918. This Journal, February, 1918.

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GAIN IN WEIGHT DURING TANNING PROCESS. PELT WEIGHT = 100.

	Section Nos. 1	5	6	2	3	7	8	4
	Tannage A	N	A	N	A	N	A	N
Acetic acid No. 1	12.3	11.4	12	11.6	14.4	12.8	13.9	13
Acetic acid No. 2	10.1	10.2	11.6	9.9	9.5	10.5	11.5	10.7
Sulphuric acid No. 3	14.2	12.7	12.2	12	16	14.2	19.6	17

ACETIC ACID EXPERIMENT NO. 1.

	Test 1 Section Nos. 1	5	6	2	Test 2 Section Nos. 3	7	8	4
	Tannage A	N	A	N	Tannage A	N	A	N
Water	14.00	14.00	14.00	14.00	14.00	14.00	14.00	14.00
Total solubles	17.31	15.87	19.11	16.89	19.14	17.27	18.72	16.75
Non-tans	2.34	2.44	2.33	2.11	2.16	2.16	2.39	2.31
Tannin	14.97	13.43	16.78	14.78	16.98	15.11	16.33	14.44
Hide substance	42.39	43.59	42.33	44.21	40.46	43.55	38.64	42.05
Combined tannin	26.3	26.54	24.56	24.9	26.4	25.18	28.64	27.20
Degree of tannage	62.04	60.88	58.02	56.32	65.25	57.82	74.12	64.68
$\frac{\text{Pelt weight} \times 100}{\text{Green weight}}$	115.6	114.3	118.1	118.5	111.1	113.4	124.3	126.4
$\frac{\text{Leather weight} \times 100}{\text{Green weight}}$	78.79	74.03	79.18	74.2	71.92	68.57	68.32	64.49
$\frac{\text{Leather weight} \times 100}{\text{Pelt weight}}$	68.17	64.78	67.04	62.61	64.73	60.46	55.0	51.0
Hide substance in pelt	28.89	28.24	28.38	27.68	26.26	26.33	20.93	21.44
Fats	1.23	1.35	0.93	0.98	0.22	0.27	1.03	1.32
$\frac{\text{Soluble tannin} \times 100}{\text{Total tannins}}$	36.27	33.6	40.59	37.24	39.14	37.5	36.31	34.68

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Acetic Acid Experiment No. 2.

	Test 1 Section Nos. 1	5	6	2	Test 2 Section Nos. 3	7	8	4
	Tannage A	N	A	N	A	N	A	N
Water	14.00	14.00	14.00	14.00	14.00	14.00	14.00	14.00
Total solubles	15.48	14 83	14.86	14.07	12.63	13.27	14.92	14.69
Non-tans	1.95	1.9	1.88	1.58	1.68	1.75	1.94	2.34
Tannin	13.53	12.93	12.98	12.49	10.95	11.52	12.98	12.35
Hide substance	44.12	45.56	44.78	46.06	45.73	46.0	44.48	45.94
Combined tannin	26 40	25.61	26.36	25.87	27.64	26.73	26.6	25.37
Degree of tannage	59.84	56.21	58.86	56.16	60.44	58.11	63.03	55.22
Pelt weight × 100 / Green weight	122.1	116.6	112.5	123.0	109.7	118.7	147.8	132.6
Leather weight × 100 / Green weight	77.32	71.62	71.62	72.89	60.17	61.03	66.28	58.65
Leather weight × 100 / Pelt weight	.63.3	61.3	60.54	59.26	54.83	51.37	45.38	43.87
Hide substance in pelt	27.93	27.96	26.94	27.29	25.14	23.62	20.17	19.4
Fats	1.46	1.04	1.03	1.05	0.21	0.2	0.53	0.35
Soluble tannin × 100 / Total tannins	33.8	33.55	32.99	32.56	28.38	30.12	32.8	32.72

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Sulphuric Acid Experiment.

	Test 1 Section Nos.				Test 2 Section Nos.			
	1	5	6	2	3	7	8	4
	Tannage				Tannage			
	A	N	A	N	A	N	A	N
Water	14.00	14.00	14.00	14.00	14.00	14.00	14.00	14.00
Total solubles	19.73	17.07	20.26	16.85	16.94	14.20	19.53	17.10
Non-tans	2.72	2.02	2.63	2.55	1.54	1.53	2.27	1.55
Tannin	17.01	15.05	17.63	14.30	15.40	12.67	17.26	15.55
Hide substance	40 16	43.32	40.04	43.78	41.44	46.05	27.73	42.24
Combined tannin	26.11	25.61	25.70	25.37	27.62	25.75	28.74	26.66
Degree of tannage	65.01	59.12	64.18	57.94	66.65	55.91	76.17	63.11
$\frac{\text{Pelt weight} \times 100}{\text{Green weight}}$	118.7	119.0	116.9	118.8	123.8	121.2	138.2	142.0
$\frac{\text{Leather weight} \times 100}{\text{Green weight}}$	85.66	77.22	84.88	75.73	76.81	68.52	77.86	71.08
$\frac{\text{Leather weight} \times 100}{\text{Pelt weight}}$	72.17	64.9	72.61	63.74	62.14	56.55	56.33	50.04
Hide substance in pelt	27.89	27.57	27.01	27.5	25.64	25.95	20.94	20.54
Fats	2.18	2.35	1 58	1.84	0.58	0.65	1.5	1.36
$\frac{\text{Soluble tannin} \times 100}{\text{Total tannins}}$	39.45	37.01	40.69	36.05	35.8	32.9	37.52	36.84

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TENSILE STRENGTH TEST.

Experiment	Tannage	Section	Original dimensions: Breadth	Thickness	Area	Stress in pounds: Total	Per sq. in.	Total elongation Per cent.	Moisture Per cent.
Acetic acid No. 1	Normal	4 D	1.531	0.25	0.3827	1820	4755	36	13.62
	Acid	8 D	1.62	0.252	0.4082	1350	3307	38	13.9
Acetic acid No. 1	Normal	7 B	1.551	0.214	0.3319	1240	3736	41	14.1
	Acid	3 B	1.541	0.234	0.3605	1000	2773	37.5	14.01
Acetic acid No. 1	Normal	7 D	1.543	0.207	0.3194	1220	3819	38.8	14.1
	Acid	3 D	1.536	0.217	0.3333	1030	3090	33.3	14.01
Acetic acid No. 2	Normal	4 X	1.642	0.212	0.3481	540	1551	38	13.72
	Acid	8 X	1.645	0.234	0.3849	610	1584	34	14.24
Acetic acid No. 2	Normal	7 X	1.55	0.157	0.2433	680	2794	43	14.13
	Acid	3 X	1.65	0.165	0.2722	600	2204	37.5	14.37
Acetic acid No. 2	Normal	7 L	1.55	0.172	0.2666	670	2513	38.8	14.13
	Acid	3 L	1.556	0.171	0 266	660	2481	37.5	14.37
Sulphuric acid No. 3	Normal	7 T	1.559	0.249	0.3881	1150	2963	45.8	14.19
	Acid	3 T	1.528	0.233	0.356	820	2303	26	14.5
Sulphuric acid No. 3	Normal	7 H	1.651	0.252	0.3933	1060	2695	43	14.19
	Acid	3 H	1.525	0.280	0.427	940	2201	21	14.5

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against these solubles having any value as a constituent of leather.

Six duplicate tests were made in these experiments and a total of twelve pairs for comparative purposes. The total solubles are higher for the acid processes in eleven out of the twelve pairs. If the combination between hide substance and tannin be perfectly stable under conditions as laid down by the extraction process, then the total solubles must be the residue from the tan liquors held by capillary forces in the leather when it is hung up to dry. The amount of soluble matter would depend on the volume and concentration of the solubles in that tan liquor which is retained by the leather under conditions mentioned above. The slight difference in the thickness between the acid and normal leather would not have any great influence on the amount of soluble matter removed when the leather is washed. A glance at the tanning process will show that the concentration of the liquor remaining in the leather should be approximately constant for each pair, so that we must now prove that the volume of the liquor retained by capillary forces was greater for the acid leather, or doubt must be felt as regards the stability of the combined hide substance and tannin.

WATER ABSORPTION TEST.

DRY LEATHER = 100.

Tannage	Acid	Normal	Acid	Normal
Number	3	7	8	4
Acetic acid No. 1	62.5	74.4	81.1	103%
Acetic acid No. 2	99	110	130	135%
Sulphuric acid No. 3	79.3	127	100.4	102%

The volume of the liquors will always be proportional to the interspaces of the leather. The hide sections increase in weight during the tanning process, but this increase is not equal to the amount of combined tannin and total solubles, so the difference must be due to water expelled from the leather. We find that a greater percentage of water has been expelled from the acid sections, and if the interspaces in the leather have decreased to a corresponding amount we would expect to find it confirmed by the water-absorption test. The amount of water absorbed is lower for the acid sections and, therefore, we assume that the volume of liquor held by the leather was proportionately lower for the acid sections and consequently the total solubles should

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be lower. The percentage of non-tans in the total solubles is lower for the acid leather in nine out of the twelve single tests, and in this as in previous experiments we have noted the small percentage of non-tans in various leathers. Such a result may be due to the non-tans decomposing much more quickly than the tannin or it may be due to the hydrolysis of the leather.

We have shown the soluble tannins as a percentage on the total tannins in the leather and in eleven out of the twelve the results are higher for the acid tests. If it be possible to remove the combined tannin with water, then these results seem to indicate that as the fixed tannin increases, the stability of the combined hide substance and tannin decreases.

The sulphuric acid plumped leather (first test) contained 0.57 per cent. of free sulphuric acid as shown by the Procter and Searle method of analysis. This is a bad result from a practical standpoint but we could probably have removed all the free sulphuric acid with sodium acetate or calcium carbonate used in conjunction with the drum process. As the concentration of the acid is increased in the pelt the resulting leather becomes harder and more rigid, the elasticity decreases, the amount of fixed tannin increases, and also the resistance to the penetration of water. From the commercial standpoint it is a desirable process, giving greater weight and stouter leather, but under conditions obtaining in a hot dry climate it is probable that the resistance to wear decreases.

The actual tanning process probably ceases when the fiber is permanently set, a result obtained with a liquor containing a low concentration of tannin. Any increase of tannin obtained after that point is reached can only act as a filling agent and the good results obtained from chrome sole leather show that there are better filling agents than the vegetable tannins. A considerable amount of leather is struck through in the pits and then placed in the drum to be filled up with extract, etc. The weak point in this process is the filling agent. The tanner's process is a correct one but the material with which he is supplied is not good. What is wanted is a substance insoluble in water and one that will remain plastic when the leather is dry.

Our work confirms some of the previous results obtained by J. R. Blockey.

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THE SWELLING OF GELATIN.*

By Hugh Garner Bennett, M. Sc.

In recent years, 1911-1917, a series of papers by Prof. H. R. Procter have appeared on this subject, accounting for the swelling of gelatin in dilute acids as due simply to the establishment of an equilibrium of osmotic pressures, the pressure causing swelling being due to the union of a strongly ionized salt within the jelly, formed by the combination of the acid with basic groups of the gelatin molecule. Now the experimental facts are not in dispute, and the vast amount of experimental data provided by Prof. Procter are a most valuable addition to our knowledge. In regard to the interpretation of these facts, however, there is perhaps room both for discussion and divergence of view. Indeed Prof. Procter has himself recognized[1] that there were alternative theories possible, and he adopted the chemical combination— ionization—osmotic pressure hypothesis largely on account of its sufficiency and simplicity as compared with the "more complicated and less verified theories depending on surface "tension and other forces, and involving the unproved and rather gratuitous assumption of a two-phased structure of the jelly."

Now it is precisely this alternative theory that the author wishes in this paper to elaborate and defend. Whether it is less or more complicated than the osmotic pressure theory is doubtful, but in either case this has little relevance to its truth. Whether the theories involved are less verified than the ionization theory is also open to dispute, though the dispute is beyond the intention of the present paper. Inasmuch as the whole fabric of modern chemistry of the colloid state depends upon the idea of heterogeneity in colloid sols and gels, the dismissal of this theory as an "unproved and gratuitous assumption" seems a very sweeping condemnation of the views and work of many eminent chemists. Moreover, as Prof. Procter is constrained to admit the two-phased structure of other colloids, or other gels (*loc. cit.* p. 327), and even of the melted gelatin jelly (*loc. cit.* p. 324), it would seem rather that the one-phased theory was the gratuitous assumption.

* J. S. L. T. C., February, 1918.

[1] J. C. S., 1914, Trans., 313. This JOURNAL, May, 1914.

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It is not questioned that, on the assumptions made by Prof. Procter, his explanation is "consistent with" the facts, but it is suggested that the alternative theory, so definitely "discarded," is equally consistent with the facts, and is entitled to a hearing. Indeed this alternative view—more complicated, less verified, unproved and gratuitous though it may be—is now widely accepted as the theoretical basis of most work on colloid chemistry, and appears to be the only generalization which reasonably correlates the facts of colloid behavior. If this alternative theory then, should present a better prospect of harmony with the general phenomena of imbibition in gels, such as gels which are not proteins (*e. g.*, the carbohydrate agar-agar), and the gels which swell in liquids other than water (*e. g.*, rubber in ether or pyroxylin in alcohol), it is the more entitled to serious consideration. It is the object of this paper to present briefly this discarded alternative, and to advocate its claim to account for the phenomena associated with the swelling of gelatin.

The point of view here adopted, therefore, is that a gelatin jelly is a two-phased structure quite analogous to that now generally supposed for all colloid sols and gels, involving a "disperse phase" of minute particles distributed throughout the "dispersion medium" or "continuous phase," that it is a lyophile system, *i. e.*, has a marked affinity between the two phases, and that the swelling and contraction of the gel is due mainly to two influences (1) the lyotrope influence of substances in the external solution, which after diffusion into the gel, cause changes in the compression of the dispersion medium, and (2) the adsorption by the disperse phase of electrically charged ions.

1. The Compression of the Continuous Phase.

Owing to the contractile force of surface tension, it is concluded that the surface layer of a liquid is under very great pressure, much greater than the bulk of the liquid. Any extension of the surface of the liquid naturally causes a corresponding extension of the proportion of liquid which is thus compressed. If in a beaker of water there be placed a porous substance, such as animal charcoal, there is a great extension of the surface of the water, and a corresponding increase in the amount of compressed water. If instead there be substituted a large

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number of very small particles of a substance, a still further increase in the amount of compressed water is involved. As the specific surface (*i. e.*, surface area per unit volume) of the substance inserted is increased, and its amount, the proportion of compressed and denser water increases also, until it is a practically appreciable percentage of the total volume. It is clear also that the extent of the zone of compression will be determined also by the interfacial tension, *i. e.*, by the nature of the substance with which the water is in contact at its surface.

Now in a gelatin sol we have the necessary conditions for a system in which the compressed water bears a considerable ratio to the total, owing to the enormous surface developed by the minute particles of the disperse phase and to the unusually wide zone of compression surrounding each particle. It should be pointed out that these zones of compression do not involve any abrupt transition from the zone of non-compression, the layer nearest the particle is under the greatest pressure, and the concentric layers under less and less pressures, the actual compression being thus an inverse function of the distance from the particle. Now if there be a gradual increase in the concentration of the sol, the time will come when these zones of compression begin to come in contact, and the system will then show a considerably increased viscosity. With further increase in concentration the zones of compression will overlap throughout the system, and when the layers under considerable pressure are thus continuous the whole system will acquire a rigidity much greater than water and approaching that of a solid body. This is a gelatin jelly. With increasing concentration the jelly becomes increasingly rigid, and if it be eventually dried out under suitable conditions it forms what is practically solid body—gelatin—which, however, still contains from 12 to 18 per cent. of water.

It will be clear that, in the case of gelatin jellies (*e. g.*, of 3-10 per cent. strength), an increase in temperature will cause an increase in the kinetic energy of the particles and effectively reduce the zones of compression. Indeed they may be reduced to such an extent that they are no longer in contact and the rigidity due to the continuous contact of the layers of great compression will then disappear, as we say usually, the jelly melts. On cool-

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ing, the decreased kinetic energy of the water molecules results in the return of the state of compression, with rapidly increasing viscosity and eventual gelation; as we say usually the jelly sets. In a jelly therefore, there is a continuous network of water under great compression, and in this network are zones of still greater compression, which surround the particles of the disperse phase—the gelatin itself, and zones of less compression which in a weak gel, at any rate, have a compression equal to or much the same as the normal state of compression in water.

One consequence of this system, is that when a piece of gelatin swells, there is a considerable enlargement in the zones of compression; in other words some, at least, of the imbibed water is compressed. Now the compression of water means that work is done, and when gelatin swells, therefore, we expect—and actually find—that heat is liberated. Hence also we expect—and find—that gelatin swells best in *cold* water. Further, the compression of water involves a decrease in volume, and we therefore expect—and actually find—that the volume of the swollen jelly is appreciably less than the volume of gelatin plus the volume of water imbibed.

Another consequence of such a compressed system is that a gelatin jelly even in water, will have a surface tension, just as the water itself has such a tension, to the water vapor above the liquid. This interfacial tension of the jelly will of course have a contractile effect, and will tend to resist swelling and to limit it as far as it possibly can. This force tending to contract the jelly and resist imbibition is therefore, one of the main influences at work in the swelling of gelatin, and is one of the two principal factors which determine the extent of the maximum swelling when equilibrium is established. The force tending to resist swelling is, in the ultimate, just surface tension. Its actual magnitude depends, of course, mainly upon the extent of compression in the dispersion medium of the gel, and will be a resultant which is a function of this compression. The magnitude will thus vary with the average compression in the continuous network of compressed water. It will be obvious that as the jelly swells the power of resisting the swelling will decrease, and the interfacial tension with the external water will tend to disappear. If the force tending to swell were great enough the swelling would

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continue until the zones of compression were no longer in contact and the gel would become sol.

As suggested above, it is probable that the extent of the zones of compression is determined by another factor in addition to the great development of surface. That factor is connected if not identical with that power which makes the system lyophile, and is evidently connected also with the solubility of the disperse phase, and may indeed be electro-chemical forces tending to form a series of hydrates, or at least to cause an orientation or definite arrangements of the water molecules in the zone of compression. This idea receives some support from the hydrate theory of solution, and the zones of compression and orientation are the colloid analogue of the hydrates supposed to exist in solutions of electrolytes. The extension of such zones on cooling are then analogous with the series of hydrates formed, for instance, by manganese chloride with 2, 4, 6, 11, or 12 molecules of water when crystallized at temperatures of 20°, 15°, —21°, —30°, and —48° C. respectively the idea being that the salts most hydrated in solution crystallize with most water.

As the compression is the result of two factors, one of which depends upon the nature of the disperse phase, we expect—and find—in other lyophile systems a considerable variation in their power of gelation. Some indeed, though very viscous, never quite set like gelatin, and others (*e. g.*, agar-agar) set to a stiff gel from a much weaker sol than gelatin. When the zones of compression are large, as in gelatin, the magnitude of the compressing force on the outermost part of the zone is relatively small and it is not surprising that time is necessary for the victory of this force over the kinetic energy of the water molecules. Hence we find a 5 per cent. jelly sets readily on cooling, but its elasticity increases steadily for many hours after it has set. This phenomenon, known as hysteresis, we should expect—and find—to be much more marked in a case where the zone of compression is unusually large (*e. g.*, an agar gel). We should also expect—and find—that hysteresis is more marked in a high grade gelatin than in a low-grade gelatin where both eventually form gels of equal elasticity. We should expect too—and we find—that hysteresis is more prominent in weak gels than in strong.

There are also other facts and considerations which have an

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important bearing upon the point under discussion. It is necessary ultimately to regard true solutions of electrolytes and other bodies as heterogeneous, though perhaps of a rather different order. From this point of view molecules and ions existing in an aqueous solution will present a surface and have associated zones of compression analogous with those suggested for the minute particles of gelatin. Hence we expect—and actually find—that in all cases aqueous solutions are less compressible than pure water, and that these solutions have surface tensions greater than that of water. Similarly such solutions have usually a greater viscosity than pure water. Now if the various substances are arranged in order of their influence on the numerical values of these various physical properties of water, the sequence is the same for each of these properties. Moreover, we find that in a large number of reactions in solutions, which are markedly influenced by the presence of foreign substances, the same sequence is observed; especially is this the case for hydrolytic actions, such as the inversion of cane sugar and the hydrolysis of esters. This sequence, known as the lyotrope series, has also a very prominent effect in influencing the behavior of the lyophile colloids, and the importance of this lyotrope influence in leather manufacture has been emphasized in a previous communication.[1] Now the swelling of gelatin (and other gels) is most profoundly influenced by the presence of substances in the external solution, and in the case of neutral substances the order of their effect is lyotrope. From the point of view adopted in this paper, this is only to be expected. If a gel comprise a continuous zone or network of compressed water, as suggested above, the presence of other substances in the gel which cause increases or decreases in the compression must modify accordingly the properties which depend upon this state of compression, such as the viscosity of the melted gel, the rate of gelation, the elasticity of the gel, and the rate and extent of its imbibition. This indeed we find to be the case. Now the substances which affect the compressibility, surface tension, etc., of water *least, i. e.*, the substances producing little or no compression of water, are just those which reduce the compression of water in a gelatin jelly, and cause a decreased viscosity, elasticity, surface tension, etc.,

[1] *J. S. L. T. C.*, Nov. and Dec., 1917. This JOUR., March, 1918.

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and which, therefore, naturally allow the gel to swell more than in pure water. Conversely, the substances which cause the greatest compression of water, the greatest increase in its surface tension and viscosity, are also the substances which increase the compression, viscosity, elasticity, and surface tension of gels, and which therefore, hinder imbibition. The effect on swelling is as follows:—

Sodium-sulphate > tartrate > citrate > acetate ; > alcohol > glucose > cane sugar ; (water) chlorides-potassium < sodium < ammonium ; < sodium-chlorate < nitrate < bromide < iodide < thiocyanate.

As the amount of compression will depend upon the amount of substance, we expect—and find—that the effect is usually additive, and that suitable mixtures of substances having an effect in the opposite sense will produce no change.

The interpretation of lyotrope influence is of course somewhat speculative, but considered as a surface phenomenon, the surface specific of the molecules and ions of the lyotrope substance must be one of the factors involved. One naturally also connects the effect with solubility and the tendency to form hydrates in solution, the zones of compression being zones of orientation and of electro-chemical attraction. The hydrate theory of solution again affords an instructive commentary. The fact that broadly speaking the polyvalent anions and the monovalent anions also group themselves together, suggests that electrical forces are at work, and the order of effect of monovalent anions almost suggests that what are called "residual valencies" are in operation. It is difficult to resist the conclusion that in the lyotrope influence, in the crystallizing of salts, and in the formation of a gel, we have zones of compression and orientation which are manifestations of the same forces—surface and electrical; the chief differences in the case of gelatin being that the zones are larger and that the electrical effect is of less definite magnitude.

However these things may be, the fact of water compression determines the rigidity of the gel, and *the changes in this compression of the continuous phase determine the surface tension resultant which hinders swelling, and which is one of the two main factors fixing both the rate at which gelatin swells, and the final volume attained by the gel.*

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Before leaving this point, it is desirable to note the effect on the swelling of gelatin of the extremes of this lyotrope influence. Substances like iodides, thiocyanates and urea prevent a gelatin sol from setting to a gel at all, and a piece of gelatin in such solutions swells rapidly until it solates. On the other hand, sulphates, tartrates, etc., make a stiffer gel on account of the enhanced compression. Gelatin in such solutions may swell, but at a much slower rate than in water and with a decreased maximum extent. A gelatin gel may in such solutions not only fail to swell at all, but actually contract and indeed be practically dehydrated. If a gel be in a very concentrated solution of such a substance, it may be that the lyotrope compression in the external solution is greater than the compression in the dispersion medium of the gel; in which case the surface tension effect is reversed, and the external solution tends to increase in volume and the gel to contract. Hence we find that the saturated solutions of such substances as ammonium sulphate and potassium carbonate will dehydrate a gel almost completely, and will also, by a similar action on pelt, make a kind of white leather. It is important to remember this contractile effect of strong solutions of salts, because in considering our present problem it is very easy to confuse this effect with a similar result produced in another manner, *viz.*, by a reduction of the force tending to swell.

2. Adsorption by the Disperse Phase.

In a previous communication,[2] the view was adopted that a gelatin gel (or hide gel) possessed an electric charge as a result of the adsorption of electrically charged ions by the particles of the disperse phase. The enormous specific surface possessed by this phase renders it particularly liable to such adsorption. This view harmonizes well also with the general behavior of colloid sols and gels, in endosmosis, kataphoresis, precipitation, etc. According to this point of view the particles of the disperse phase are surrounded by a surface layer in which thse ions are in much greater concentration than in the volume concentration of the dispersion medium. The hydrion and hydroxyl ion are particularly liable to such adsorption. In the case of a lyophile colloid, like gelatin, the charge may be either positive or negative, according to the nature of the predominant ions in the

[2] *J. S. L. T. C.* Dec., 1917. This Jour., March, 1918.

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dispersion medium, and the amount of adsorption is determined by the concentration of these ions in accordance with the adsorption law.

In effect, therefore, the particles of the disperse phase each carry an electric charge of the same nature, and as similarly charged bodies repel one another, the particles of the disperse phase will tend to separate and to occupy a bigger volume. *It is suggested that this repulsion of similarly charged particles is the cause of the swelling of gelatin.* The amount of charge and force—tending to swell—is due possibly to several ionic adsorptions, which may be considered to operate independently, and the power of repulsion is determined by the net charge, which in the case of a "positive colloid" is positive, and in the case of a "negative colloid" is negative. As ions possess different electric charges, the charge on the disperse phase is subject to the valency rule.

Now the repulsive force between two similar and similarly charged bodies is proportional to the amount of charge and is inversely proportional to the square of the distance between them. The amount of charge on a colloid particle will be determined by the dispersity—best signified by the specific surface (s)— and by the operation of the adsorption law $y = mac^{\frac{1}{n}}$. The distance between the particles varies with the degree of swelling, and is determined by the cube root of the volume of the gel (v). Hence if F be the force tending to make the gelatin swell, we may write

$$F = \frac{\theta}{d^2} = \frac{s\ y}{v^{\frac{2}{3}}}$$

Now with all electrolytes, even with water, we have both positively and negatively charged ions and y is consequently determined by the difference in the amounts adsorbed. Hence in the case of an electrolyte with an equal number of oppositely charged ions $y = ma^1 c^{\frac{1}{n_1}} ma_2 c^{\frac{1}{n_2}}$, where a_1, a_2, and n_1, n_2 are the appropriate constants for the particular ions concerned. Hence at constant temperature, pressure, etc., we may write

$$F = \frac{s\ m\ (a_1 c^{\frac{1}{n}} - a_2 c^{\frac{1}{n}})}{v^{\frac{2}{3}}}.$$

The force tending to make a piece of gelatin swell is proportional

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to its mass, which is perhaps fairly obvious. The swelling force is also an inverse function of the volume of the gel, and as swelling proceeds, therefore, the force tending to swell further decreases. The force tending to swell is proportional to the specific surface of the disperse phase, other factors being constant. To illustrate this one has only to imagine that one particle of the disperse phase be split into two particles each carrying half the original charge. It is clear that a new repulsive force becomes operative, which did not before influence the swelling, and that the distance between the particles is halved. In the swelling of gelatin, however, we may consider the dispersity constant for constant temperature, and if we consider unit mass we see that the force causing swelling depends upon the operation of the adsorption law and upon the degree to which the gel is already swollen.

In the swelling of (say) 1 gram of gelatin to its maximum, both the contractile force of surface tension and the expanding force of electrical repulsion are in operation. At the commencement the latter is much the greater force—hence the rapid imbibition. Both these forces decrease in magnitude as the swelling proceeds, but the force tending to swell decreases at a more rapid rate, and the time comes when it has decreased to the precise value of the force tending to resist swelling. At this point equilibrium is established and the maximum swelling attained. Obviously this maximum will in many cases be determined largely by the value of $a_1 \dot{c}^{n_1} - a_2 \dot{c}^{n_2}$. This factor, therefore, demands particular consideration.

Now unfortunately, the adsorption law constants for the different ions have not yet been numerically determined, so that we are still somewhat in the dark as to the operation of ionic adsorptions. It is possible, however, to form conclusions of a qualitative or relative order, and these are such as to throw much light upon the question at issue. In the first place we know that in general the various ions are not usually very widely different in the extent to which they are liable to be adsorbed. If this were otherwise, the valency rule would hardly operate so well in endosmosis, kataphoresis, and precipitation. In consequence we must expect the differences between the ions to appear in small

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rather than in large concentrations, the amounts adsorbed being under those conditions more affected by changes in the volume concentration. At the larger concentrations, therefore, the value of $a_1\dot{c}^{n_1} - a_2\dot{c}^{n_2}$ is small, and the force causing swelling often tends to zero.

There are, however, noticeable differences at lower concentrations. Thus we know that if a substance be primarily a positive colloid, it will adsorb kations more readily than anions. As gelatin falls into this class we may, therefore, conclude that usually $a_1 > a_2$. Further, it often happens that very adsorbable substances are less affected by concentration changes, and in the case under consideration, therefore, we should expect that $n_1 > n_2$. Moreover, we know that the hydrion and hydroxyl ion are much more readily adsorbed than other ions, *i. e.*, have a large value for a. Hence in the case of gelatin we expect that $a_1\dot{c}^{n_1} - a_2\dot{c}^{n_2}$ will have a comparatively large value when one of the ions is H^+ or OH^-. Also we know that organic anions are usually much more strongly adsorbed than inorganic anions, and hence that in such cases a_1 is more nearly approached by the value of a_2. It should be emphasized perhaps, at this point that these various considerations are not based upon any facts relating to the phenomena of imbibition in gels, or in gelatin in particular, but are based upon the behavior of colloids in endosmosis, kataphoresis, electrolytic precipitation, adsorption, etc.

Now if we select a few simple figures which are in accord with the above considerations, we can examine the value of the factor $a_1\dot{c}^{n_1} - a_2\dot{c}^{n_2}$ in a purely illustrative and typical way, and at any rate form some idea as to the manner in which it is likely to vary. The figures might be:—

Ion	n	a
Hydrion *or* hydroxylion	20	10
Kation of a metal	15	7
Organic anion	10	8
Inorganic anion	6	6

For the sake of simplicity we can assume that these ions are all monovalent. The ions adsorbed by unit mass will then be

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10c 1/20, etc. If these hypothetical adsorption isotherms be plotted as usual, we get the fairly typical curves shown in Fig. 1.

FIG. I

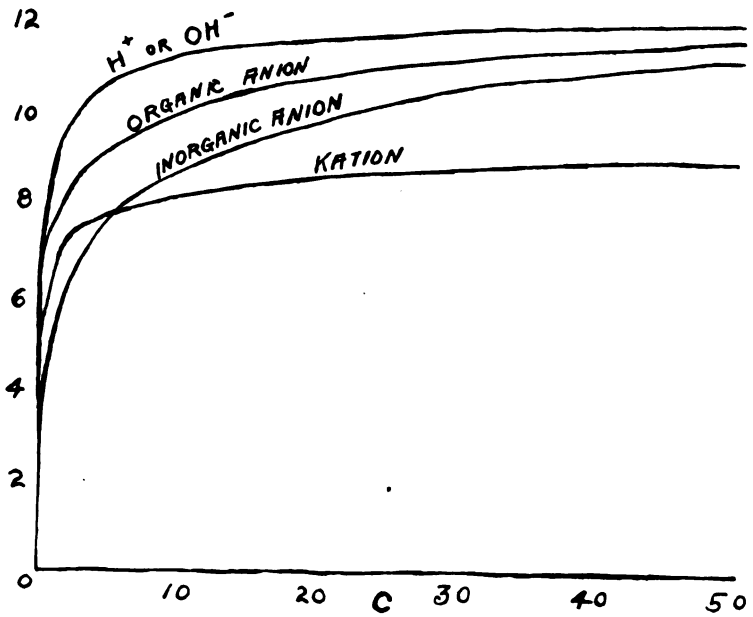
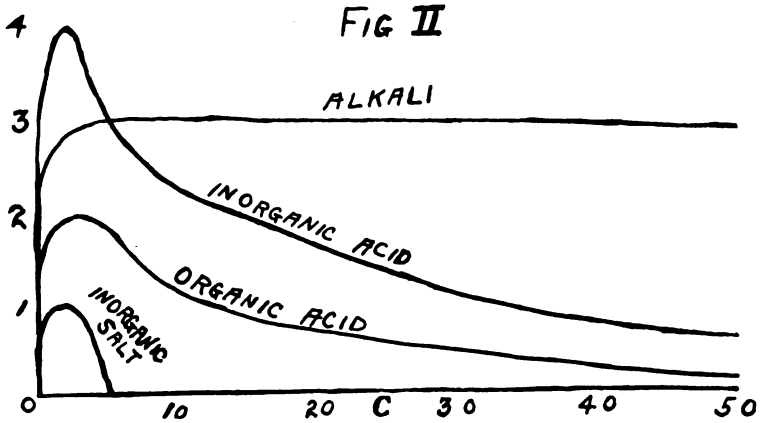


FIG II



Now in practice there are always two of these ions, each giving

its own specific effect in opposite senses, and the difference $(a_1^{n1} - a_2^{n2})$ represents the net charge adsorbed. Hence we have the following combinations:—

Inorganic acid	$10C\ ^1/_{20} - 6C\ ^1/_6$
Organic acid	$10C\ ^1/_{20} - 8C\ ^1/_{10}$
Alkali	$10C\ ^1/_{20} - 7C\ ^1/_{15}$
Inorganic salt	$7C\ ^1/_{15} - 6C\ ^1/_6$

If we plot these values of net adsorption against the concentration we obtain the curves shown in Fig. 2.

On the assumption that the net charge adsorbed is the dominant factor in determining the maximum swelling at equilibrium, one must, therefore, regard the curves of Fig. 2 as representing the changes in volume of the swollen gel as the concentration is increased. Now in *type* these curves correspond to those obtained by experiment from hydrochloric acid, acetic acid, caustic soda, and common salt. The maximum swelling with hydrochloric acid increases rapidly with the concentration at first and then rapidly decreases, though not at such a great rate. The swelling with acetic acid increases less rapidly and to a less maximum, but decreases more slowly. With common salt there is a slight swelling followed by contraction. Caustic soda gives a rapid increase in volume at first, afterwards much less so, and finally yields an exceedingly slow decrease. The correspondence of these facts with the type-curves inevitably suggests that the phenomenon of swelling might be accounted for, in part at least, along these lines.

Of course it is not likely that the simple figures selected for the illustration of the argument are either relatively or absolutely correct. Thus we know that the adsorption curve for hydrions and hydroxylions are not likely to be quite identical, as assumed above. As gelatin is primarily slightly positive, it is probable that the values of a and of n for hydrion adsorption will be relatively slightly greater. The relative values supposed, however, are near enough to illustrate the contention that the type of the maximum volume curve can be explained on this assumption of different adsorption isotherms for each of the ions.

If the remarks in Section I on the compression of the continuous phase be recalled, it will be obvious that in the present sec-

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tion we have been giving the question of equilibrium-volume a rather one-sided consideration. The volume of the gel when equilibrium is established may be determined in type by the net charge adsorbed by the disperse phase, but it will be modified also by the lyotrope influence of the particular substance on the continuous phase. When gelatin swells in solutions the influences on both phases are always in operation, and either upon occasion may become predominant. In the case of neutral organic substances, such as cane-sugar, the lyotrope influence is the determining factor. In the case of neutral salts the predominant influence is decided by the place occupied by the salts in the lyotrope series. If at either end of the series the lyotrope influence is uppermost and the effect of ionic adsorptions is practically swamped. Thus sodium sulphate and sodium iodide hinder and promote imbibition respectively as could be expected from their strong lyotrope power. On the other hand, in the case of sodium chloride, which has very feeble lyotrope influence, the relatively different adsorptions of its ions comes to the fore. With acids and alkalies the relatively large adsorption of the hydrion and hydroxylion causes this to be the predominant influence, but we must concede the possibility that purely lyotrope influences may be at work in some cases, and especially at the greater concentrations. Indeed it is sometimes a difficult problem to decide whether an increase or decrease in swelling is due to lyotrope or adsorptive influence, but broadly speaking, we can expect strong lyotrope effects at either end of the series and also at large concentrations, and we can expect strong adsorptive effects in dilute solutions, in the middle of the lyotrope series and in the case of alkalies and acids.

DISCUSSION.—Having reached the conclusion that the swelling of gelatin is mainly influenced by changes in the compression of the water of the continuous phase, and by changes in the adsorption of ions by the disperse phase, it is both interesting and instructive to make comparison with the alternative theory advanced with such power by Prof. Procter. In doing so there appear many more points of contact and approximate agreement that would at first sight be expected from such different assumptions.

In the first place there is the common idea that the gel has

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a network structure. Prof. Procter suggests that it is a network of gelatin, while herein it is suggested that the network is compressed water. In this connection it is interesting to bear in mind that theory of lyophile colloids which considers each component to exist in both phases, *i. e.*, that a gelatin sol or gel consists of globules of a concentrated solution of gelatin dispersed in a weaker solution of gelatin. On this view the network must consist both of water and of gelatin.

In the second place there is a full agreement between the two alternative views as to the magnitude of force causing swelling. Herein that force is ascribed (in dilute acids) to the excess positive charge due to the greater adsorption of the hydrion, which caused the gelatin particles to repel one another. Prof. Procter ascribes the force to the osmotic pressure of the acid anion. While there is here perhaps a radical difference, it is noteworthy that the electric charges involved, though of opposite sign, are equal in magnitude.

In respect of the force resisting swelling there seems little point of contact. The author has found it somewhat difficult to realize what this force is, according to Prof. Procter's view, but it is evidently something quite different from what is herein suggested inasmuch as it increases with the swelling according to Hooke's law, whereas from the writer's point of view it decreases with the swelling according to the interfacial tension between gel and external solution.

In regard to the question as to whether the gelatin "chemically combines" with or "adsorbs" the acid of the external solution, little ink need be spilled. Between a chemical combination which is slightly hydrolyzed in dilute solution and an adsorption in which the values for a and n is large, the difference is practically speaking small. Adsorptions cannot be always due solely and entirely to surface tension considerations, electro-chemical attractions must in some cases also come into play, and if so, a and n will be large. It is very possible that gelatin is such a case and that Prof. Procter has discovered one of the connecting links between adsorption and chemical combination.

There remains the question of the one or two-phased structure of the system. After all, homogeneous and heterogeneous are relative terms. Colloid sols are more heterogeneous and solutions

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are more homogeneous. Strictly speaking, both are ultimately heterogeneous, but if lyophile colloids are chiefly amicrons, which seems probable, then the difference between the two views now being discussed is just this: that it is herein suggested that the disperse phase consists of particles with a diameter of the order of 10^{-7} centimeters, and that Prof. Procter suggests molecules with a diameter of the order of 10^{-8} centimeters, but possibly polymerized.

Whichever of the two views discussed above, proves eventually to be the more fruitful, it is the hope of the writer that the discussion will to some extent contribute to the hammering out of the truth. In problems so difficult and yet so important there seems room for more than one method of attack.

THE SWELLING OF GELATIN.*—(A REPLY.)

By Henry R. Procter.

I have carefully gone through Mr. Bennett's paper[1] with a view to friendly criticism, but find it very difficult to know what to reply to. We have attempted (and successfully as Bennett himself admits) to devise a theory of the swelling of gelatin with acids and bases on the well-established and fundamental grounds of osmotic pressure, the mass-law and ionic dissociation, while he prefers one based on "adsorption," "lyophil," "lyophobe," and "lyotrope" substances, terms which he does not profess to define or explain by known chemical and physical causes. It is of course easy to account for anything by the assumption of sufficient unknown properties (witness the services of "vital force"), but the invention of pretty Greek words does not explain anything, or carry us much further in really scientific knowledge. It is also much easier to produce plausible qualitative hypotheses than to define them in mathematical formulae which can be numerically tested and which embrace all the known phenomena of the particular reaction.

With regard to Bennett's claim that gelatin jellies and sols are two-phased systems (emulsion-colloids), there is no need to waste many words, since it is merely a question of size of par-

* *J. S. L. T. C.* March, 1918.

[1] *J. S. L. T. C.* February, 1918; This JOURNAL, June, 1918.

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ticles. In a sense, everything is two-phased or many-phased; globules are made up of molecules, molecules of ions, and ions of electrons, but according to the original phase-rule definition, phases are things which can be mechanically separated. Even the ultra-microscope gives no proof of mechanical structure in a gelatin gel or sol, and all that we claim is that the particles are so small that they come within the range of chemical and molecular attractions, and hence are capable of chemical reactions.

Against one statement, however, I must raise energetic protest, though I know that Bennett is supported by respectable textbook authorities. Surface-tension is not the *cause*, but a relatively small *effect* of the enormous internal pressures of liquids due to molecular attraction; and far from the surface layer being a region of compression, it is one of tension and lessened density. There is every reason to believe that the boundary between a liquid and its superincumbent gas or vapor is not an abrupt one, but a gradual transition through a very thin layer of that "critical" state which lies between the liquid and the gas. Internal pressures differ from those in the interior of the earth mainly because molecular attractions, however intense, are of short range, and diminish much more rapidly than that of gravitation, but the principles are the same. A stone on the surface of the earth is drawn downwards with its maximum weight, but subject to no superincumbent pressure. In the center it would suffer enormous pressure, and great increase of density, but would have no weight. Equally, the attraction drawing a molecule *inwards* is at a maximum on the surface, but as it suffers no pressure from without, its compression is at a minimum.

This statement, however, refers solely to the true *surface*, and an *interface* of contact with a solid or another liquid is under different conditions. Where the attraction of the molecules of each liquid for the other is less than for its own, a surface is still formed, but with a lessened tension, since a part of the attraction is exerted on the molecules of the second liquid instead of being wholly resolved in the plane of the surface. If the mutual attractions are equal to or greater than the individual ones, complete mixture or solution takes place. At the interfaces with insoluble solids, mixture cannot take place, but the

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surface tension of the liquid may become negative and tend to extend instead of contract, as for instance paraffin oil does on metals. No known means exist of measuring either the surface-tensions of solids, or their mutual tensions with liquids, but it may be inferred that the former are very high, and the latter often negative. How this may affect the Willard-Gibbs theory of adsorption I have never seen discussed, but it may account for some of the so-called "anomalous" adsorptions, though others are probably chemical or electrical. On the other hand the interfacial tension between a gelatin gel and a weaker gelatin sol is possibly *nil*, and necessarily very small, so that any seriously condensed zone between them is very improbable, and evn if it existed would hardly account for rigidity, as no experimental condensations of liquids by pressure or the solution of salts seem to cause very large increase of viscosity. If these facts are admitted, much of the basis of Bennett's theory disappears.

Procter and Wilson attribute the swellings force of the jelly to the osmotic pressure or kinetic energy of ions associated with the colloid, while Bennett ascribes it to the static electrical repulsion of similarly charged particles; the charge being due to an assumed preferential adsorption of + or — ions. (This preferential adsorption, if it exists, has nothing to do with the Willard-Gibbs adsorption-law, but must itself be due to chemical affinity.)

We of course admit that colloidal particles have usually electrical charges due to ions, but, at least in the case of organic colloids, attribute them to Donnan's "membrane" or surface "potentials" which are produced when one of the ions is not diffusible into the outer liquid. These potentials are small, and merely surface-effects, the whole system being in electrical equilibrium.

Assuming, however, that the particles are actually charred, they will not repel each other directly as Bennett assumes, but their charges will be balanced by the attraction on their surface of a layer of ions of the opposite charge, so that the whole complex will be electrically neutral. This is Helmholtz's theory of the "double layer," and in electrophoresis the particles move because this layer is continuously displaced in the opposite direction to the particle. There is one way, however, in which electric charge may lead to a compressed water-layer round a particle, of which

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Bennett must have the benefit, though it is probably much more important in relation to the higher charges of suspension colloids. A charged particle, say of gold, must collect round it a shell of ions of the opposite sign, but in pure water the only ions are $H^{\cdot}$ and OH', and these are very few and in equilibrium with unionized water by the ionization law, and in order that the particle may be surrounded by a sufficient layer of one of them to balance its charge it must attract a relatively thick layer of water. On the addition of an electrolyte, other ions are supplied in much more concentrated solution, the layer of water thins off, and the sol precipitates; the more rapidly, the higher the valency of the added ions. The same effect must theoretically occur with emulsions, but as their charges are much lower, it is probably almost negligible unless the electrolyte solution is concentrated.

I agree with Bennett that the lyotrope series is of practical importance in tanning, though we know little of its theoretical meaning. It is, as he says, possibly connected with the formation of solvates, conjugates of water with the dissolved salt, which withdraw water from the solution and so increase its concentration. Wilson's work (*J. A. L. C.*, 1917, 12, 446) on the effect of neutral salts on chrome liquors seems to indicate such an effect, and his Table I. (*Loc. cit.*) follows the lyotrope order as far as it goes, but my information on the formation of solvates with different salts is too small to test its theoretical significance. If Bennett will devote himself to obtaining more exact figures on this subject, he will be performing useful service.

There are, of course, many interesting points in his paper to which I have not alluded, but I have already occupied more space than the JOURNAL can well spare, and must therefore defer their consideration.

THEORY OF COLLOIDS.*

By W. Harrison, M.Sc.

J. A. Wilson,[1] has attempted to apply to colloids generally the theory of the equilibrium between hydrochloric acid and gelatin

* *J. S. L. T.C*, March, 1918.

[1] *J. A. C. S.* October, 1916; this JOURNAL, April, 1917.

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as first put forward and developed by Procter in conjunction with his students.

He draws attention to the similarity of the formula $z = \frac{1}{4cx + e^2}$ with the generally accepted empirical formula for adsorption (using the same system of notation) $z = kx^{1/p}$ where p represents a constant, usually about 2 so that generally $z = k_1 \sqrt{x}$.

Now z in Procter's equations is the concentration of ions bound to the colloid by electrochemical attractions. Whereas in experiments on adsorption the concentration z represents the total concentration of substance adsorbed by the colloid.

Using the same notation as in Procter's equations the total concentration of substance adsorbed is $a + y + z$, and if it is required to deduce the adsorption law mathematically methods other than those adopted by Wilson must be used.

The author has made the necessary calculations, which are given below, and it will be seen that the quantity c, so very important in all Procter's work, is not required.

At equilibrium in the external solution.

$$x = [H+] = [Cl^1].$$

In the jelly phase:

z = concentration of gelatin ions.

a = concentration of non-ionized gelatin chloride.

$y = [H^+]$.

g = sum of concentrations of gelatin, gelatin chloride, and gelatin ions.

V = volume of jelly in cubic centimeters.

From the law of equality of products.

$$x^2 = y(y + z). \qquad (1)$$

From the laws of ionization.

$$z(y + z) = Ka. \qquad (2)$$

From (1)

$$z = \frac{x^2 v^2}{y}, \qquad (3)$$

and

$$y + z = \frac{x^2}{y}, \qquad (4)$$

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substituting 4 in 2 we get

$$a = \frac{zx^2}{Ky}, \tag{5}$$

by adding (4)

$$y + z + a = \frac{x^2}{y} + \frac{zx^2}{Ky}, \tag{6}$$

let $m = y + z + a$

substituting (3) on the right-hand side of equation

$$m = y + z + a = \frac{x^2}{y} + \frac{(x^2 - y^2)x^2}{Ky^2}. \tag{7}$$

From (7) we get the equation

$$(mK + x^2)\, y^2 - Kx^2y - x^4 = 0.$$

The roots of this equation are:

$$y = \frac{x^2}{2}\left\{\frac{K \pm \sqrt{K^2 + 4mK + 4x^2}}{mK + x^2}\right\}.$$

Attempts to get m in terms of x resulted in equations containing powers of x up to the fourth which could not be solved.

Except in very dilute solutions where secondary ionization takes place $g = a + z$, in fact, this assumption gives mathematically the same result in Procter's equations, as neglecting the constant K^1.

$$g = m - y.$$

$$g = m - \frac{x^2\,(K \pm \sqrt{K^2 + 4mK + 4x^2})}{2mK + 2x^2},$$

since $g = \frac{1{,}000}{MV}$ M being the molecular combining weight.

the above equation gives us a means of ascertaining whether the amount of a substance adsorbed by a colloid is in agreement with the laws of electro-chemical equilibria.

This equation fits in very well with Procter's work in gelatin which is also in close agreement with a formula of the type used empirically for adsorption phenomena, but neither equation can be derived mathematically from the other.

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BOOK REVIEW.

THE PHYSICAL CHEMISTRY OF THE PROTEINS. By T. Brailsford Robertson, Ph. D., D. Sc., Professor of Biochemistry and Pharmacology in the University of California. 483 pp. Price $5.00 net. Longmans, Greene & Co., New York.

Whatever may have been the original intentions of the author, it would require only a change of title to convert this book in effect into one volume of an extensive treatise on the chemistry of leather manufacture, which to a large extent is the physical chemistry of colloidal systems, in all of which, proteins constitute at least one component. This book will therefore add very materially to the literature dealing with leather chemistry.

In his preface the author points out that "if we were to endeavor to interpret the behavior of the proteins solely in the light of preconceptions derived from the study of the chemistry of the metals, for example, or the simpler organic compounds, we would find that the behavior of the proteins displays merely a bewildering variety of inconsistencies. Their 'amphoteric' character, their multiple basicity and acidity, their instability in aqueous solution and, above all, the enormous mass and catenary configuration of their molecules confer upon them properties which are comparatively unfamiliar in other fields of chemistry, or else exaggerate properties which are normally displayed by the simpler chemical bodies only to a comparatively negligible degree."

Referring to colloidal behavior he says: "To describe a particular property or mode of behavior as a 'colloidal phenomenon' neither defines nor interprets it and furthermore fails even to describe it, since there are no phenomena which are distinctively 'colloidal' and displayed by every member of the colloid group, saving only those phenomena which depend primarily upon the simple factor of the mass or volume of the molecules, and which are therefore predictable from and implied in the properties or behavior of the smaller molecules of the non-colloidal substances. Similarly, the use of the term 'adsorption' to describe the union between colloids and other substances implies a uniformity where no uniformity exists and is, moreover, devoid of utility or meaning unless we attach to the definition some distinct idea of the nature of the underlying forces which condition the union, whether these forces be regarded as consisting of chemical (*i. e.*, atomic) attractions or of capillary (*i. e.*, molecular) attractions."

Two schools of opinion have developed over the question as to whether or not we are justified in assuming that Avogadro's rule is applicable to protein solutions. The author's own views follow:

"In this work I have endeavored to interpret the physico-chemical behavior of the proteins in the light of the laws of Boyle and of Gay-Lussac, as they have been applied to solutions by Van 't Hoff, and of the Guldberg and Waage mass-law which, as Larmor has shown, is a direct consequence of Avogadro's rule and Boyle's law. I have also assumed the validity, in protein systems, of the first and second laws of heat, albeit the

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applicability of the second law of heat to protein systems has, in some quarters, been questioned. In considering the *electrochemical* behavior of the proteins I have assumed the applicability of Arrhenius' hypothesis of electrolytic dissociation, of Kolrausch's law of the independent motion of ions, of the Nernst theory of concentration-cells, and further, although this has of recent years been very strongly questioned, the applicability of the Guldberg and Waage mass-law to reactions between ions. I believe that the utility of these hypotheses justifies us in applying them until still more useful hypotheses shall have been elaborated to amplify or replace them."

The book itself is divided into four parts, the first dealing with the chemical constitution of the proteins, their preparation in the pure state, their quantitative estimation, and with their compounds. The electrochemistry of the proteins forms the subject matter of the second part and includes discussions of the formation and dissociation of protein salts, the combining capacity of the proteins, the electrical conductivity of solutions of protein salts, and the electrochemistry of coagulation. The third part deals with the physical properties of protein systems and the fourth with chemical dynamics in protein systems, including studies in hydrolysis and synthesis of the proteins by enzymes.

The author presents a theory of the ionization of protein salts which is especially deserving of attention, not only because of the author's extensive use of it, but also because of its bearing upon theories of pickling and of tanning. Many writers have considered the amphoteric nature of proteins to be due to their amino and carboxyl groups. Thus a protein could neutralize either acid or base:

$$H_2N.R.COOH + NaOH \rightleftharpoons H_2N.R.COO' + Na^+ + H_2O$$

$$HOOC.R.NH_2 + HCl \rightleftharpoons HOOC.R.NH_3^+ + Cl'.$$

In each case a protein salt being formed which yields but one protein ion. The author admits having been formerly inclined to this view, but states that an accumulation of data irreconcilable with this view led him some years ago to abandon it. His present theory assumes the action to be of the nature expressed by the following equations:

$$R - N = \overset{\displaystyle OH}{\overset{|}{C}} - R + NaOH \rightleftharpoons R - \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle H}{\overset{|}{N''}}}} + R - \overset{\displaystyle ONa}{\overset{|}{C^{+}}},$$

$$R - N = \overset{\displaystyle OH}{\overset{|}{C}} - R + HCl \rightleftharpoons R - \underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle H}{\overset{|}{N''}}}} + R - \overset{\displaystyle OH}{\overset{|}{C^{+}}}.$$

Where in both cases only protein ions are formed. Although the argu-

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ments given in favor of this view are numerous, they do not appeal to me as convincing, excepting perhaps in the case of the statement that the compounds which proteins form with HCl, for example, when dissolved in water, are excellent conductors of electricity, and true electrolytes, yet they do not yield chlorine ions. However, I should require a somewhat stronger proof than has been given that this statement holds true for proteins in general.

In referring to Procter's work on the acid-gelatin equilibrium, the author contends that according to Procter's view no equilibrium would result, "since the acid anions and the free acid itself could not simultaneously be equal in concentration within and without the jelly." In the recent publications on this subject it is shown that this very fact is responsible for the equilibrium and for the peculiar swelling curve. The author would reconcile the apparent difficulty by assuming that the protein-acid compound yields no inorganic ions and that the swelling of the jelly is due to the osmotic pressure of the colloid particles themselves, which being unable to penetrate the colloid network in which they are entangled necessarily compel the compensating migration of water. However, it is not shown how this theory can account for the repression of the swelling by further addition of acid.

The chapters on the hydrolysis of proteins and of polypeptides should be of great value to those interested in the chemistry of the beamhouse processes.

Considered from the standpoint of the leather chemist the book is an extremely valuable addition to the literature and one which has been much needed, for I know of no other book which supplies the same material in a form so suitable for the student of leather chemistry. In a subject of such vast scope and complex nature, it is but natural to find some doubtful statements, but the book is replete with ideas and information of unquestionable value to the development of the science.

JOHN ARTHUR WILSON.

ABSTRACTS.

Outline of Colloid Chemistry, III. W. D. BANCROFT. *J. Franklin Institute*, **185**. 373-387 (1918; cf. This Journal **13**. 125 and (1918). In this paper four more divisions of the main subject are given along with 112 references.

Types of Precipitates.—The author distinguishes eight types of precipitates: *Crystalline*, such as is obtained by neutralizing KOH solutions with H_2SO_4; *colloidal* or non-settling, one in which there is little or no agglomeration like that formed by mixing very dilute solutions of Pb $(NO_3)_2$ and K_2CrO_4; *flocculent*, one obtained by the agglomeration of a non-settling, non-gelatinous precipitate to a bulky mass, like AgCl formed by mixing suitable solutions of $AgNO_3$ and KCl; *curdy*, which results when a flocculent precipitate agglomerates to a fairly dense mass, a typical case being the precipitate obtained by adding acids to

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caseine; *sandy*, resulting when a curdy precipitate agglomerates to a dense mass, like the alumina obtained from hot sodium aluminate in the Baeyer process; *gelatinous*, involving the agglomeration of a hydrous and viscous precipitate to a bulky form as results from mixing concentrated solutions of $Ba(SCN)_2$ and $MnSO_4$; *jelly-like*, differing from a gelatinous precipitate in that the liquid phase is not visible as such; and *fluid*, a precipitate too mobile to be classed as gelatinous, as is obtained by adding an excess of HCl to sodium oleate.

Theory of Peptization.—A stable colloidal solution contains very fine particles kept from agglomeration by a protecting film of some sort, electrification being equivalent to a film. By peptization is meant the disintegration of large masses into such particles, especially when done chemically, as opposed to mechanical or electrical disintegration. Certain solutions peptize certain precipitates forming colloidal solutions and this is always the result of adsorption. Theoretically there are three possibilities: If an adsorbed film has a low surface tension on the water side and a high one on the other side, it will tend to scrunch up and to peptize the solid as internal phase; if the reverse be true, the solid will tend to form the external phase; while if the two surface tensions are equal, neither will prevail. A theory of peptization follows at once from Freundlich's view that adsorption always lowers the surface tension. We may have peptization by a liquid, a non-electrolyte, an adsorbed ion, a salt, or by a peptized colloid. When a liquid is adsorbed by a solid, it will tend to peptize it. Water peptizes tannin. Gelatin is not peptized by cold water, but is by warm water. In some cases mixed solvents will peptize a solid much better than either alone. Freshly precipitated AgCl is peptized by $AgNO_3$ or KBr, the silver and bromine ions being strongly adsorbed. Many oxides are peptized by their chlorides or nitrates forming basic salts. Sulphides are peptized by H_2S. Gelatin is peptized by KI. Water peptizable substances like gelatin, dextrin, soap, or saponin peptize many precipitates and are called protecting colloids because they prevent the agglomeration and settling of finely divided precipitates.

Condensation Methods of Preparing Colloidal Solutions.—These are divided into six classes and illustrated. 1. *Reduction without Electrolysis*: at 50° hydrogen gas reduces silver oxide in contact with water liberating the metal in the colloidal state. 2. *Reduction with Electrolysis*: When very dilute solutions of gold, silver, or mercury are electrolyzed, some of the metal comes out in colloidal form. 3. *Oxidation*: The reaction between H_2S and SO_2 yields colloidal sulphur. 4. *Hydrolysis*: Colloidal solutions of hydrous ferric oxide can be made simply by boiling dilute solutions of ferric chloride. 5. *Metathetical Reactions*: Concentrated colloidal arsenious sulphide solutions can be prepared by the action of H_2S upon As_2O_3. 6. *Decomposition by Light*: Colloidal solutions can be obtained when substances are precipitated by light as in gold or sulphur solutions.

Dispersion Methods of Preparing Colloidal Solutions.—Five types are described. 1. *Removal of Agglomerating Agent*: If AgCl precipi-

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tates be washed at once the silver salt is apt to run through the filter when the excess of soluble electrolyte has been removed. Likewise zinc sulphide is apt to form a colloidal solution when the ammonium salt is washed out. *2. Addition of a Peptizing Agent*: Instead of washing out a precipitating agent, one may add a peptizing agent, for example sulphides are readily peptized by H_2S. 3. *Mechanical Disintegration*: When reduced to an impalpable powder by long grinding, quartz can be converted into colloidal hydrous silicic acid merely by boiling with water. 4. *Electrical Disintegration*: The disintegration of noble metals with the formation of colloidal solutions results when a direct current arc is formed under water between two wires of the metal, using 30 to 40 volts and 5 to 10 amperes. 5. *Electrochemical Disintegration*: With a lead cathode in caustic soda solution, the lead disintegrates when the current density exceeds a critical value, and the solution is colored black like ink with fine particles of metallic lead, which is due to the temporary formation of a lead-sodium alloy, which is subsequently decomposed by the water

J. A. W.

Tanning in the Philippines. C. E. Bosworth. Special agents, Series No. 161, Department of Commerce.

The hides are mostly from the carabao, a species of buffalo, from the native cattle, somewhat similar to the Indian cattle, and from the horses and ponies. Skins are obtained mostly from goats with a few from sheep.

The hides from the native cattle are of a very good quality but the skins are usually in very poor shape.

Leather manufacture in the Philippines is important only to the islands. None of the locally tanned leather is exported. Altogether there are about 175 tanneries devoted almost exclusively to the tanning of sole and undressed heavy leather. The total output probably does not exceed 95,000 hides per year. The industry is wholly in the hands of Chinese and native Filipinos.

The tanning machinery in the Philippines is limited to a bark mill in one tannery and a sole leather roller and three drums in another. Just at present the roller and the drums are not in use. The latter tannery is managed by a graduate of the Leather Sellers' Technical College, of England, and in time will undoubtedly develop into a modern plant. Primitive methods, probably brought to the islands by the Chinese, are still in use.

Most of the tanneries are in the open air, or merely sheltered by a thatched bamboo roof. When the hides are received they are laid in packs of 17 or 20 and soaked for about eight hours. This soaking is usually done in the river. For liming they are put into pits usually built of masonry and arranged in a series of 3 or 4 to as many as 20. These pits are of a practically standard size, 5½ feet long, 3½ feet wide, and 3 feet deep. Sometimes they are built above ground and sometimes partly below. The liming solution is made by mixing 25 liters (about 3 pecks)

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of lime in nearly enough water to fill the pit. A cane or bamboo sieve is used to remove lumps and stones from the lime. The hides are then folded lengthwise, hair out, and placed in the pit one on top of the other until the pack is complete. They are left in the lime 10 to 15 days and during that time are handled three or four times. The pack is inverted at each handling.

Unhairing and fleshing are usually done by a workman who stands in the water of the river and works on the hide laid over a bamboo beam. This is a slow process because the bamboo beam is narrow and the flesher works toward himself. The beam is generally at too high an elevation to be convenient. The fleshings and cuttings are mixed with the lime, dried, and sold for glue stock. The proceeds are usually equally divided between the tanner and the workmen.

The tan pits are of practically the same construction as the lime pits but a little larger. The tanning liquor is made of chopped camanchile bark (25.36 per cent. tannin) mascerated for three days in a mixture of two-thirds fresh water and one-third used liquor. The strength of the liquor thus made is uncertain, for no measuring instruments are used. The proportion of bark used is 250 to 300 pounds to 1,200 liters (317 gallons) of liquid. After soaking for three days, the bark is removed from the pits and the hides put in. A layer of bark is left on the bottom onto which a hide is placed flesh side down. Then a layer of bark is placed over the grain side and half of the hide folded over. This process is repeated until the vat is filled, each hide and the whole pack being treaded down by the nearly naked workman who lays the pack. This treading is repeated often during the first few days to hasten the penetration of the hide by the tanning liquor and to prevent putrefaction. The hides are then left in the tan pits for about six weeks. It is said that if the leather is not to go to market immediately the hides are placed in vats containing old used liquor and left indefinitely—sometimes for years.

In preparing the tanned hides for market they are spread on a platform, where natives scrape the water and tanbark from them and smooth the surface as much as possible. Then they are stretched on bamboo sticks and quickly dried in the full glare of the tropic sun. This is all the treatment they receive at the hands of the tanner. The user dresses them to suit his individual requirements.

The temperature is so high, the action of the tanning material so slow, and sometimes the hides in such poor condition, that many of them are lost by putrefaction. So far, no process has been found by these tanners to overcome this difficulty. It is quite possible that the use of extracts with the bark would eliminate much of the trouble. In only one tannery are the hides suspended in the vats and in only one tannery are extracts being seriously considered. Cleanliness and better water would also have a beneficial effect.

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The leather resulting from these crude methods is naturally very inferior. The poor grade of lime, the temperature, filth, and crude methods all tend to destroy hide substance.

The Chinese are the only tanners producing light leathers. These are simply the result of splitting heavy hides, usually carabao. The splitting is done with a thin, axe-shaped knife operated by hand. The operation is insufferably slow but the workmanship is wonderful.

The leather is used almost wholly by the native and Chinese shoemakers, who buy it from native and Chinese leather dealers, to whom it is sold by the tanners.

The Philippine Islands are well supplied with raw tanning materials. Chief among them are camanchile and mangrove barks. There are a number of other barks, but they are either too low in tannin content or insufficient in supply to be commercially important.

Camanchile bark is the favorite tanning material among the tanners of the islands. It contains about 25 per cent. tannin and produces a light-colored leather. The tree is found in nearly all parts of the islands, though its growth is scattered. It is neither systematically cultivated nor conserved. Camanchile tan liquor quickly ferments in the Philippine climate and creates a strong disagreeable odor. This bark will probably never be of commercial interest or importance outside the islands. About 1,500 tons are used annually by local tanners. Two or three years ago the bark was purchased from the native collectors at $10 a ton, but the price has recently risen to $35 per ton.

The Philippines have mangrove swamp areas estimated at 800 square miles. There are 21 species of mangrove, or 2 more than are credited to Borneo, the great cutch-producing island. While nearly all the islands of the archipelago have considerable growths of mangrove, the swamps of Mindoro, Mindanao, and Palawan are of greatest commercial importance, and none of them are being worked at present for tanning material.

The swamps of Mindoro are only 12 hours distant by steamer from Manila, are large in area, and practically virgin. Many of the swamps in the northern islands have been pretty well cut. It is estimated that the Mindoro swamps will yield about 50,000 tons of bark. The swamps of Mindanao extend along the coast for 45 miles and it is estimated that about 90,000 tons of bark are available here. Extensive lumbering operations are being carried on in Mindanao now, but the lumber companies do not use the bark at all.

The Absorption of Sulphuric Acid by Wool by W. HARRISON, M. S. T., Society of Dyers and Colorists, March, 1918. The author found that wool absorbed sulphuric acid from a 5 per cent. solution on boiling, but that the acid could be completely removed by repeated extractions with boiling water.

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Tanners Institute *News, Bulletin* No. 36. The class of 1918 in Tanning and Applied Chemistry have just finished their annual tour of inspection.

The students and instructors visited tanneries and manufacturing plants in Detroit, Grand Rapids, Grand Haven, Whitehall, Milwaukee, Waukegan and Chicago.

Strephonema Kernels. The *Leather World,* March, 1918. These kernels obtained from the Belgian Congo contain about 38 per cent. fat melting at 29°C. The meal obtained after the extraction of the fat contains about 31 per cent. tannin which, however, gives a dark purple red color.

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VOL. XIII. JULY, 1918 NO. 7

THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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Journal of the

American Leather Chemists Association

Vol. XIII JULY, 1918 No. 7

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W. A. FOX . . . . . Associate Editor

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CHANGES OF ADDRESS.

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PRESIDENT'S ADDRESS.*

By C. R. Oberfell.

It is with great pleasure that I call this, the fifteenth Annual Meeting of our Association, to order. Last year the meeting took

* Read at the Atlantic City meeting of the A. L. C. A., May 16, 1918.

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place shortly after our country entered the great war, and during that meeting the thought often came to me as to what effect the war would have on our 1918 meeting. I felt that in the nature of things this meeting would be considerably curtailed in attendance and in the good accomplished. Although it is too early to predict, the indications are that this meeting will be more successful than I then thought.

I do not know how many of our members have joined the armed forces, but I do know that many of them have, during the past year, acted in an advisory capacity to the Government as experts in their line. Several at the present time occupy official places, and of them we are justly proud.

Since our last meeting a number of events have transpired which will doubtless have an important bearing on the chemistry of leather, in fact, on the leather industry. I have in mind, first, the organization of the American Leather Research Laboratory. Such a laboratory has long been the ambition of the leaders of the leather industry, and has received the support and active co-operation of the American Leather Chemists Association. The National Association of Tanners will receive the commendation of every thoughtful man, and I have no doubt but that this laboratory will surpass the hopes of those who have contributed towards its organization and support. Exceedingly few industries have shown such foresight in providing for the application of science to its manufacturing problems. The director of this laboratory has been selected, the equipment is being assembled and installed as fast as conditions permit, and before long the staff will be actively at work.

Another event to which I wish to refer is the formation from the nations allied against Germany of the Society of Leather Trades' Chemists. As the war has progressed and revealed more and more the barbaric tendencies of the German Government, it has become increasingly evident to the leather chemists of the Allied Nations that future amicable relations with the Germans in the International Association of Leather Trades Chemists are impossible. They, accordingly, have withdrawn from the old and organized this new society, and have extended a friendly hand to the A. L. C. A. We certainly wish them success and, in turn, extend our hand of friendship to them. There has been pro-

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posed to our membership, in the shape of a change in our By-Laws, a plan for the mutual co-operation of the two societies, which permits an interchange of journals to those desiring it. I trust that this proposal will receive your support at this time.

Public appreciation of the important place which applied chemistry occupies in the industries has been emphasized during the war. The step which the leather industry has taken in the organization of a Research Laboratory indicates that this industry intends to avail itself of all possible advantages which science offers. Progress in this direction must follow along two distinct lines,—one through this Research Laboratory and the other through the work of the laboratories connected with each plant. Both are necessities. The tanners have taken all the steps that are possible to assure the success of the Research Laboratory, but I wish to contribute a thought that applies to the plant laboratories and plant chemist that will assure success on this side as well. I need not go into details to explain why the success of the plant laboratories lies in the ability of the chemist in charge; it is a simple truth that such is the case. The only way to obtain chemists of ability is to pay them such salaries as will attract men of sound education and training to the leather field. If this is not done, other industries will take the men with brains away from us, and we can have what is left. I speak of this because I believe the tendency in the leather industry is to pay plant chemists entirely too small salaries, and this question has become increasingly important on account of the general awakening to the value of applied chemistry in manufacturing. Well trained chemists to-day are a great scarcity, and if the leather industry wishes to continue in the forefront of progress, it will have to revise its opinion on this point, or else it will open its eyes some day to find that other industries have acquired the men with the best brains. But, after all, is it not always the wisest policy to do well anything that is worth doing at all, and how else can this scientific work be done well except by men of ability? Perhaps some of the disastrous experiences of tanners in the past with their chemists can be attributed to the condition that they were not willing to pay the price for securing men above the mediocre class. I venture to predict that if the tanners will loosen their purse strings in order to employ the best men that

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can be obtained, that the dependence of the leather industry on chemistry will rise to the same plane of importance and necessity as in other chemical industries with which we are familiar.

Often times the best meaning people fall into a mental error and, by advancing their ideas, cause damage where they hope to do good. I am sure that everyone will agree with me when I say that the "trade press" of the leather industry has been progressive, and has always fought for the advancement of science in the tannery. For this reason, I wish to take this occasion to comment on an editorial which recently appeared under the caption "Ask the Chemist."

> "When the leather goes wrong, ask the chemist. That's the real rule of tanning these days. Time was when, the leather going wrong, the boss and his friend held an inquest on it, thumbed it, chewed it and discussed it, and then burned it and tried their luck again, but these days if the leather goes wrong, the boss hurries a few specimens of it to the chemist, who gets out his glasses, his test tubes and his acids, and studies the leather like an auditor studying the books, until he finds out what is the matter with it. Then he tells the boss, and the boss guides his next tannage accordingly. It costs a bit, perhaps to call the chemist, just the same as it costs a bit to call the doctor, but it saves a lot of time, money and worry in the long run."

This is the wrong view of the value of the chemist. Why wait until the patient is about to die before calling in the doctor? Doesn't it seem wiser to let the doctor keep in such close touch with a patient as to be able to detect any serious disturbance of his system and thereby avoid the resulting illness? The true and most valuable function of the chemist is to follow the processes of manufacturing by the aid of his knowledge of "chemical control" so as to detect harmful conditions and to take measures to prevent the "leather going wrong" long before the tanner suspects that everything is not right. "Chemical control" should not only be a police force in the tannery, to act as a sort of a mystic detector of someone failing to follow instructions, but should be a linking of the scientific and practical in such manner as to maintain chemical processes moving along in a normal and uniform manner, and to take strict account of the efficiency of the processes and the economy of operation. If the leather industry wishes to reap the full benefit from science, it must recognize the above truth and relegate to a place of less importance the

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idea that the chief value of the chemist lies in controlling purchases of raw materials, important as this is, or as a means of enabling those in authority to make sure that subordinates are conducting the various processes according to instructions.

We have met here to discuss in joint sessions with the National Association of Tanners problems growing out of the war. The war and its problems touches all of us in our daily existence, and it is natural that subjects of war prominence should occupy largely the attention of this meeting. Then too, there has been less research work undertaken during the past year, due to the fact that everyone has been busier than ever before with problems of a routine nature.

It has been four years since we have had the pleasure of meeting with our friends, the tanners, and we appreciate their willingness to come and discuss common problems with us.

It gives me pleasure to extend the welcome of the A. L. C. A. to the tanners, and also to the members of the Morocco Manufacturers' National Association, the Patent and Enameled Leather Manufacturers' Association, the National Association of Importers of Hides and Skins, and the National Association of Tanning Extract Manufacturers.

SECRETARY'S REPORT.

Active Members.

Active members May 1, 1917		165
New members		10
Active members resigned	3	
Active members transferred to Associate membership, by request	2	
Active members residing in Germany	3	
Active members dropped on account of non-payment of dues	2	10
Active members gained		9
Members May 1, 1917		165
New members		10
		184
Loss in members		10
Active members May 1, 1918		174

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ASSOCIATE MEMBERS.

Associate members May 1, 1917		200
New members	36	
Two transferred to Associate membership	2	38
Associate members dropped on account of wrong address	1	
Associate members resigned	2	
Associate members residing in Germany	1	4
Associate members gained	4	34
Members May 1, 1917	200	
New members	38	
	238	
Loss in members	4	
Associate members May 1, 1918	234	

TREASURER'S REPORT.

1917–1918.

Receipts.

Cash on hand May 1, 1917		$2,425.43
Dues	$2,081.52	
Interest	19.55	
On sale of first Liberty Bond, 3½ per cent	10.21	2,111.28
		$4,536.71

Disbursements.

Annual meeting expenses	$ 361.08	
Council meeting expenses	49.90	
Secretary's expenses	166.66	
Printing, postage, expressage, supplies and insurance policy	313.05	
Dues returned	$5.00	
Amount overpaid on bound volume returned	2.25	
Rebate on dues	1.00	8.25
Purchase of Liberty Bond, first issue		1,000.00
Contribution to Red Cross		200.00
From Journal Account		726.66 2,825.60
Balance on hand, in bank May 1, 1918		$1,711.11

JOURNAL ACCOUNT.

Receipts.

From advertisers	$1,469.41	
From back numbers	29.85	
From bound volumes	204.66	
From subscriptions	186.17	$1,890.09

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Disbursements.

Journals (April, 1917, to May, 1918)	$2,030.26	
Reprints	267 07	
Abstracts and translations	12.00	
Index	31.12	
Copyrighting Journal	12.10	
Bound volumes	93.75	
Editors' expenses	159.35	
Paid out for back numbers of the Journal	10.10	
Rebate on subscription	1.00	$2,616.75
To General account		$ 726.66

SUMMARY.

Cash on hand May 1, 1917		$2,425.43
Receipts, General Account	$2,111.28	
Receipts, Journal Account	1,890.09	4,001.37
		$6,426.80
Disbursements, General Account	$2,098.94	
Disbursements, Journal Account	2,616.75	4,715.69
Balance on hand, in bank, May 1, 1918		$1,711.11
Liberty Bond, second issue, 4 per cent. (First Liberty Bond converted into second issue)		1,000.00
Total		$2,711.11

Since May 1, 1918, checks amounting to $415.99 have been received.

Due from advertisers, dues, bound volumes and back numbers $1,003.58.

H. C. REED, *Secy. and Treas.*

MANUFACTURE OF OAK EXTRACT IN JAPAN.*

By Lloyd Balderston.

Among the things which I am sorry to miss this year, not the least important is the meeting of the Association. President Oberfell has invited me to send a paper to be read, and I feel more like writing a letter than a formal paper. A reason for this is the lack of material for a scientific paper. The work here at the university is new, and much of my time has been given to efforts to get apparatus and machinery installed. Very

* This article was sent to be read at the recent Annual Meeting at Atlantic City, but was received too late for that purpose.

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little work in tannin analysis has been done, because as yet we have no evaporator and dryer in working order.

The troubles encountered in this connection are typical, though more extensive than those met with in connection with any other specially ordered apparatus. The apparatus makers modify designs without consulting the designer, and so the beautifully finished pieces have to be made over before they can be used. In this case the making over was not according to order, and so the oven has to be made over a second time, and has now been waiting three weeks for the tinsmith.

I am disposed to blame many of my troubles on the language, and if, as I hope, two or three Japanese gentlemen are present at the meeting, I must here beg their pardon for saying disrespectful things about their language. To illustrate the causes of my distrust, I may cite a particular case. A telephone message in reference to my household goods, sent by freight from home, was received by the janitor. He conveyed it to an English speaking student, who told me "your goods have arrived in Sapporo." I asked him at what station in Sapporo they were. He turned to the janitor and further conversation in Japanese took place. Then he said, "They have not yet come to Sapporo, but are at Otaru." Otaru is the seaport, 20 miles away. I have had many experiences of this sort, and am inclined to think that it may be very difficult to give perfectly definite directions in Japanese.

Instead of an alphabet, the language has a syllabary, each syllable made up of a vowel sound following a single consonant. The number of these syllables is about 70, and most of them may be followed by *n*, so the whole number of possible monosyllables which can serve as words is less than 140. It is not surprising that many of these monosyllables are terribly over-worked. The number of pairs of words of similar pronunciation but different meaning is great in English, and we even have more than two in a few cases. In Japanese, in addition to all the pairs, there are many groups of ten or more words of one syllable pronounced alike but with different meanings, and represented by different Chinese characters. Japan is therefore, among other things, a paradise of punsters.

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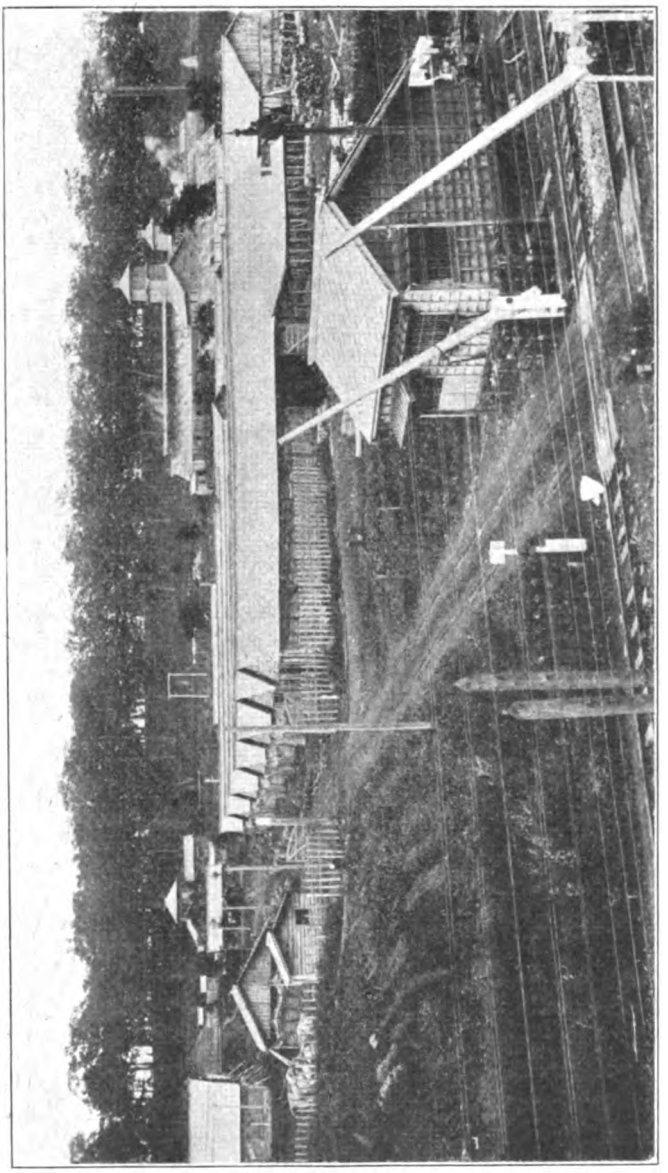

EXTRACT PLANT OF THE JAPAN HIDE AND LEATHER COMPANY, IKEDA.
(The hill in the background is covered with the tan-bark oak, *Q. dentata.*)

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The indefiniteness of Japanese ways of saying things is well illustrated by the method used to describe where a house is. Instead of naming or numbering streets, they give names or numbers to blocks. You address a letter to Mr. A., North 1, East 4. The block includes houses facing on four different streets, and the postman has to know which house in the block is Mr. A's. There is no relative pronoun, so that descriptive clauses necessitate very involved sentences. Verbs have no distinction of either person or number and nouns and pronouns none of number, so that the ideas "I am," "you are," "he is," "it is," "we are," "they are," are all expressed by the same word. Personal pronouns are little used. Some of the most used verbs have a bewildering assortment of meanings, often some of them transitive and some intransitive. Put an ending on an adjective and it becomes a verb. These are enough to indicate that Japanese is different from English, and that precision of statement is not its strong point.

The skill of Japanese artisans is great, and has been so for many generations in spite of their language handicap. The new things which have been taken up since intercourse with Europe began are done with great skill also. To cite a single example, Japanese chemical glassware is excellent. So is Japanese leather, as made by several companies. One of these, the Japan Hide and Leather Company, has tanneries at Tokyo, Osaka and Shanghai, and owns and operates a plant for the manufacture of oak bark extract at Ikeda, in the eastern part of Hokkaido, about ten hours' journey by rail from Sapporo. I had been planning to visit this extract plant in the spring vacation, and early in March I was so fortunate as to meet Mr. Nagasawa, an engineer of the company, on his way to Ikeda. He gave me a cordial invitation to visit the factory, and told the superintendent to expect me.

I had learned that there is another plant a few miles this side of Ikeda, belonging to the Nitta Company, which makes powdered extract. The authorities of the university tried to secure from the main office of the company at Osaka permission for me to visit their plant also. They declined, however, and I was obliged to be content with seeing the outside of the Nitta factory during the few minutes our train stood at the station. The fac-

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tory is surrounded by great ricks of oak wood with the bark on, which is ground for the making of extract.

In the early morning of April 2 I started for Ikeda in company with two students, a senior and a graduate student, one of whom had been at Ikeda before. The external appearance of the train in which we traveled is not unlike an American train except for the colored stripes indicating first, second and third class. The second class compartment which we entered occupied half of a car, the cushioned seats running lengthwise. This arrangement of seats rather than the American plan seems necessary because of the narrowness of the cars, the gauge of the track being about a foot narrower than our standard. Some coaches, however, have crosswise double seats on one side of the car and a lengthwise seat on the other. The locomotives used in Hokkaido are of American patterns, many of them bearing the name plate of the Baldwin Locomotive Works, Philadelphia.

The morning was misty, so we could not see far. Our way lay for an hour or more up the level valley of the Ishikari, the largest river in Japan. The scenery was mostly farms, a large part of the cultivated area being devoted to rice paddies. The skill of the Japanese agronomists in developing varieties of rice which will flourish in the latitude and climate of Boston is most remarkable.

At Ebetsu, 20 miles from Sapporo, we passed a large paper plant. I hope to have the opportunity of doing some work on their waste liquors. The woods used are all coniferous, and they are worked up by the sulphite process.

At many stations we saw huge piles of logs, nearly all pine or spruce, awaiting transportation to the markets of the South. A large proportion of these are hewn approximately square. The care which the Government exercises to keep up the supply of lumber is in evidence on the hills all about. The slopes are planted in coniferous trees, quite close together. When these are large enough for small poles, a large part are cut out. Another thinning a few years later yields larger poles, and so a small fraction remain to make saw-logs. The use of poles is very much greater than in America. Scaffolds are built of poles, lashed together with rice straw ropes. Fence posts are sections

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of poles, and floors are laid on poles which have been hewn on one side.

Farm houses and other buildings generally are of frame construction. In the city, roofs are about evenly divided between shingles and galvanized iron, and in the country between shingles and thatch. The split pine shingles are small and thin, and the roofs are not long lived.

Snow lay all about during the first half of our journey, but after we had climbed the range and passed through the tunnel at the summit, we came out into clear weather, and our view took in the great valley of the Tokachi River, bare of snow, and with a few signs of life in the vegetation. The panorama of foot-hills in the foreground, and of wide level valley in the distance as we came out of the tunnel is something to remember. It is said to be one of the finest views in Japan, and I am quite unequal to the task of describing it. The boundary of our view is formed by a low range of hills beyond the river, some 75 miles away.

An hour of winding brought us down into the valley, where we saw many farms recently cleared and still covered with stumps. Much of the timber which covered this rich bottom was oak, *Quercus dentata,* and some of the trees had not been cut, but the bark peeled up to 8 feet or so from the ground, and sold to the extract factory. This mode of destroying trees so that the land may be farmed seems wasteful and slovenly, but we must not be too critical, remembering that in our own country "deadenings" were not unheard of a generation ago.

Further down the valley the settlements are older, and we saw many prosperous-looking farmsteads. We stopped an hour short of our destination at Obihiro because of the better hotel there. Obihiro is a new town of 1,000 or more, with well-kept streets and attractive shops. Nearly all houses are of wood, and paint is in general not used, so you will quite understand that a new town looks more inviting than an old one. The natural fate of a Japanese dwelling which escapes fire and reaches the age of 15 or 20 years is to be torn down and replaced. You will get an idea of the fire risk from the fact that the annual premium rate of insurance on household goods in Sapporo is 5 per cent.!

Our hotel in Obihiro was most attractive. I had been so provident as to bring along felt slippers, as shoes must be left

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at the door, and I cannot prevent the slippers furnished for the use of guests from falling off with disconcerting frequency. Slippers are not the only articles furnished for the use of guests, and my companions were soon out of their European dress and at ease in the flowing robes of the Japanese gentleman. They wished to persuade me to spend the evening in similar garments, but I decided to wait till warmer weather to make the experiment.

We were installed in a second-story room of ample size and beautiful finish. Three sides were sliding paper-covered doors. The heat proceeded from a large bronze pot containing a charcoal fire. Furniture was limited to one small table about a foot high, containing writing materials. The floor was covered with rush mats 2 inches thick, faced with the familiar Japanese matting. The proper attitude in such a room is to sit on your feet on a cushion. Out of deference to my occidental habits, however, three chairs and a table were brought in, and a delicious meal was served in the room. At bed-time mattress-like cushions were brought in and laid on the floor for beds, and others somewhat larger and scarcely less thick served as covers. My allowance of covers was three, of which I used one.

Next morning we had breakfast in time to start at 6, in a train made up of both passenger and freight cars. The latter were mostly of the short four-wheeled English pattern. Double-truck, American style freight cars are coming into use, especially for coal. Reaching Ikeda about 7, we found the extract plant not far from the station, at the base of a wooded knoll, most of whose trees are oaks, such as furnish the bark of which the extract is made. Most of the space within the factory enclosure is occupied by bark-storage sheds. Some of the bark comes in sacks of rice-straw matting, and some in bundles, tied with ropes of rice straw. That in the sacks is winter bark, chipped off, and accompanied by a good deal of wood. The bundles are summer bark, peeled in the familiar fashion. In both cases the outer rough bark is shaved off, at least from the heavier pieces.

In spite of our early arrival, we were cordially received at the office, and the foreman showed us over the plant. The bark is taken from the sheds to the mill in hand cars, running on steel rails. The mill is a roller apparatus, crushing but not cutting the material. The largest pieces are 6 inches long by 2 inches wide.

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This preparation seems to me too coarse for the best results, but we have not yet been able to analyze the samples we brought back, so I am not sure. The crushed bark is taken by hand in small dump cars to the leach house. The buildings are so arranged against the side of the hill that these cars run on a level to the top of the leaches, which are cylindrical in shape, built of pine staves 2 inches thick, and have a capacity of about 20 tons of bark each. These leaches are eight years old and still quite sound. The eighteen vats are arranged in two sections. The liquor is pumped forward by an arrangement like a steam injector attached to each leach, which sprays the liquid over the top of the next leach. The time of extraction is about four days, and the liquor run to the pan-house averages about 30° barkometer. The pan-house equipment includes a triple effect evaporator, of familiar aspect, built by the Philadelphia Coppersmithing Company.

The standard product is a liquid extract of 30° Baumé. This ferments rather easily in warm weather, so cresol is added in the proportion of one part per thousand, which prevents fermentation and has no injurious effect on the extract. The published analysis for this extract calls for 51 per cent. total solids, 32.4 per cent. tannin, 17.7 per cent. non-tans and 0.9 per cent. insolubles. Preliminary analyses at the university laboratory showed lower purity than this, but the difference is probably due to the use of the filter-bell method of analysis in making the published analysis.

A solid extract is also made, being simply held in the third effect until the water content is reduced below 20 per cent., when the product hardens on cooling. It is run into paper lined wooden casks of about 200 pounds capacity. The published analysis of the solid extract indicates 49.8 per cent. tannin, 31.3 per cent. non-tans and 1.5 per cent. insolubles, with 17.4 per cent. water.

Near the pan-house is the cooper shop for making packages for both solid and liquid extracts. Pine casks for the solid product were being made when we were there. We also saw great piles of staves and heads for the heavy oak casks for liquid. These hold about 25 gallons. In the boiler room a mixture of coal and spent bark is burned. The quantity of steam required is less than one would expect, as the mill used requires much

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less power than a shaving mill, and no power is used for conveying machinery, so the spent bark cannot be completely used, and two small mountains have accumulated.

On our return to the office we found the manager, who was very courteous to us, telling about the source of the bark, methods of collecting, etc.. and gave figures for yearly output. He also showed us many interesting samples of leather and tanning materials, and we saw the analytical apparatus which they use. The Procter filter bell and lightly chromed hide powder are the characteristic factors of the method of analysis. The yearly output of the factory is 4,000 tons, more or less. The bark comes by rail from all parts of the valley. It does not appear whether there will be a continuous supply of bark or not. It depends on replanting oaks on hillsides and other places not available for farming. I am told that this is being done to some extent.

Tea was served in the office, and we chatted for an hour. The manager gave us samples of bark and extract, and we planned to conduct a test of the tannin content of winter and summer bark. It will be necessary for this purpose to collect samples over a long period. We departed with new evidence of the quality and extent of Japanese courtesy, and I said to my companions on the way back that Japan is the country where the men are not too busy to be polite to each other.

The return journey carried us up the mountain slope in the waning afternoon, and the snowy summits, seen first on this side, then on that, as we wound around, made a picture of such beauty as can hardly be put into words. The last four hours we travelled in the dark, and were willing to admit that we were tired when our 17 hour day ended.

HOKKAIDO IMPERIAL UNIVERSITY,
Sapporo, Japan.

THE DETERMINATION OF FAT IN LEATHER.

By L. E. Levi and Aug. C. Orthmann.

In an article by John Arthur Wilson and Erwin J. Kern, this JOURNAL XIII 138, the authors suggest using a mixture of ethyl ether and carbon tetrachloride in the proportion of equal parts, for a solvent of fat in leather, especially in vegetable tanned leather.

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The great difference between extraction with petrolic ether and the above solvent is attributed to the presence of oxidized or hydroxylated fat in the leather, either entering as such or, as in the case of some fats, oxidizing after entering the leather. In Table I a difference of approximately 25 per cent., based on the total "fat" is found.

This great difference led us to try out the new solvent on different kinds of leather.

To obtain a pure solvent: The carbon tetrachloride was first treated with "hypo soda," then with caustic soda and allowed to stand for several days after adding anhydrous calcium chloride, then finally distilled. To the ethyl ether was added anhydrous calcium chloride and the same allowed to stand for two or three days after which both solvents were mixed in the proper proportion and distilled into a flask containing anhydrous calcium chloride. About 500 cc. of the solvent was distilled at one time leaving about 25 cc. in the distilling flask.

In our first extraction we employed hemlock-tanned leather, first making the extraction with petrolic ether for a period of nine hours, then after evaporating all petrolic ether from the leather and out of the Soxhlet, extraction was continued for four hours with the new solvent mentioned above. Six samples were extracted as shown in Table I.

TABLE I.

Leather No.	Per cent. fat with petrolic ether extracted for nine hours	Per cent. extractive with new solvent extracted for four hours
1	23.38	1.43
2	33.36	1.81
3	31.15	2.14
4	25.46	1.51
5	33.54	1.67
6	32.00	1.67

These leathers were known to be fat-liquored with a small amount of sod oil, then stuffed with stearine. Ten grams of the finely cut leather were used. A seventh leather is omitted from the above table for the following reason. The bulk of the new solvent was evaporated from the extractive in an open dish over an electric hot plate in this particular case, the atmosphere immediately surrounding the hot plate being heavily laden with

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vapors of the new solvent. By some mishap or other a short circuit caused a spark and set the vapors afire, consuming a large part of the contents of the dish, without interruption. This does not agree with the statement in Wilson and Kern's article in which they state that the mixture of the two solvents, "will burn in periodic puffs."

Referring to Table I. we will only consider the nature of the new solvent extractive. Color, dark brown. No noticeable odor, no greasy appearance or feel, but hard and glassy, slightly soluble in water, slightly soluble in alcohol, partly soluble in ethyl ether, nearly all soluble in carbon tetrachloride. On burning the extractive an odor such as of burning wood was noticeable. The above characteristics suggested a mixture of oxidized fat and possibly tannin or other vegetable matter soluble in water.

To substantiate our contention regarding the soluble tannin a sample of ordinary dry quebracho extract was carefully washed with petrol ether, dried, and 10 grams extracted for eight hours with the new solvent with a yield of 0.1882 gram or 1.88 per cent. of extractive, this appeared to be very much like the extractive obtained from hemlock-tanned leather described above.

We then prepared a sample of union sole leather, about 150 grams of the sample were ground to pass through a 20-mesh sieve and well mixed to assure a uniform sample.

Table II gives the results obtained. In each case 10 grams were used for analysis.

TABLE II.

No.	14 hours extraction with petrol ether Per cent.	After evaporating off petrol and continuing extraction for 5 hrs. with new solvent Per cent.	Total petrol ether and new solvent extractive Per cent.	14 hours extraction with new solvent Per cent.
1	2.46	1.52	3.98	5.31
2	2.51	1.32	3.83	4.75*

As in the former case with hemlock-tanned leather, the new solvent extractive in this case was of a dark brown color and had an odor of overheated tannin. Where the new solvent was used

* The extractive first came over clear, but was of a slight amber color. After three hours' extracting the contents of the extraction flask were turbid and further extraction produced a flocculent precipitate which continued to increase as extraction prolonged. In this case the extractive was filtered through a dry filter before the solvent was evaporated off.

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alone, without previous extraction with petrol ether the extractive appeared oily, with dark blotches adhering to the bottom and sides of the dish. These were well washed with petrol ether and dried. The residue was found to be partly soluble in water.

This led us to extract a larger portion of the leather to more closely examine the extractive. Fifty grams of the leather were used (see Table III). First extraction with petrol ether for a period of nineteen hours. Ether was removed from the leather and Soxhlet by evaporation.

2nd extraction with new solvent for 4 hours
3rd extraction with new solvent for 4 hours
4th extraction with new solvent for 15 hours
These extractives were treated with hot water. The water insoluble was treated with absolute alcohol.

TABLE III.—Per cent. is based on original sample of leather.

Extraction	Per cent. yield	Per cent. soluble in hot water	Per cent. soluble in absolute alcohol
1st	2.490	None	——
2nd	0.912	0.318	0.594
3rd	0.296	0.188	0.108
4th	0.637	0.432	0.205
Total	4.335	0.938	0.907

The table shows that of the total extractive 21.64 per cent. is soluble in water. Of the new solvent extractive (a total of 1.845 per cent.), approximately 50.00 per cent. is soluble in water and the balance soluble in alcohol. The alcohol soluble would suggest oxidized fat, although it is possible that this portion contained vegetable matter insoluble in water, but soluble in alcohol. Oxidized fat as a general rule produces a dark brown color with alcohol. The above alcohol soluble produced a pink in dilute solution and maroon in more concentrated form.

From Tables II and III it will be noticed that the petrol ether extractions check fairly close. The same is the case with the combined extractions of petrol ether and the new solvent in Table II, however, these combined extractions do not total up to the yield where the new solvent is used alone, the greatest difference being 1.43 per cent.

Also, the new solvent extractive in Table III shows 1.845 per cent. whereas the mean in Table II is 1.40 per cent., these differ-

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ences are probably due to the length of time of extraction, that is, the longer the extraction the more the yield. The sample of leather used in Table III was not extracted further. The result obtained with four extractions convinced us that the new solvent could not be used for accurate purposes.

We next employed a number of chrome-tanned leather samples for our work. These samples were practically all of the same tannage using soap, sod oil and neatsfoot oil for the fat liquor and finished with blood albumen in the season. Results follow.

TABLE IV.

Color	Petrol ether extraction 14 hrs. Per cent.	After evaporating petrol 5 hrs. extraction with new solvent Per cent.	Total extraction Per cent.
Chocolate	5.27	1.97	7.24
Chocolate	11.70	1.29	12.99
Black	6.45	0.93	7.38
Tan	5.43	1.02	6.45
Natural chrome	6.27	1.65	7.92

The extractive from the new solvent extraction in all cases were of an oily appearance. The petrol ether extractive showed that a very slight amount of coloring matter had been extracted, but in the cases of the new solvent extractive a deep coloration was present, with the exception of the natural chrome-colored leather which was of a slight green color. This extractive had an ash content of 1.57 per cent., the larger part of which was chrome oxide. This is probably due to chrome soaps or complex organic chrome compounds formed in the leather during fat-liquoring. A large part of the extractive undoubtedly consisted of dyestuff employed in coloring the leather and should not be reckoned as fat. It is also possible that non-fatty matters such as the different finishes employed are soluble in this new solvent for fat, for example: Ten grams of commercial blood albumen were extracted for fourteen hours with petrolic ether with a yield of 0.86 per cent. of fat. This was further extracted with the new solvent for six hours with a yield of 0.91 per cent. of substance with characteristics of anything but fat or oxidized fat.

After reviewing the above results our conclusions are that the solvent suggested by Messrs. Wilson and Kern cannot be applied to all leathers, nor to all conditions that exist in the different tan-

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neries and laboratories. The time for extraction would have to be set for different kinds of leathers, depending upon the tannage and the kind of oil or grease and finish employed in making the leather. We cannot entertain the suggestion to substitute petrolic ether with this new solvent, concordant results may possibly be obtained on chrome leathers, but we doubt if all the extractive could be termed as fat or grease. This surely holds true of vegetable-tanned leather as shown in our results.

The authors feel that just criticism of a method or process will arouse enough enthusiasm to have such method or process brought before the eyes of the leather chemists in its proper light, and in that way sift out the faults and flaws that would otherwise render a method useless. We wish to express our sincere appreciation to Messrs. Wilson and Kern for their criticism of our method for the Determination of Fat in Leather as published in this JOURNAL, X, 445 (1915), however, we believe, that Messrs. Wilson and Kern have confined their efforts to rather very narrow limits by making no more than a triplicate analysis on one sample of leather with a medium fat content. In our paper, *loc. cit.* we give analyses of thirty-two different leathers in which the fat content varies from 1.31 per cent. to 35.92 per cent. We have employed this method in our laboratory for a number of years for the purpose of routine work only, but we have had many instances in which to compare both our bottle shake method and the Soxhlet method.

In September, 1917, the writers had the pleasure of Mr. J. B. Churchill's presence, (Director of the American Leather Research Laboratories) in this laboratory. During Mr. Churchill's stay here we had occasion to make comparative analyses by the two methods in question. At that time, under the eyes of a very careful and critical observer we found no fault in our method, such as mentioned in Messrs. Wilson and Kern's paper, nor since that time have we had any difficulties in obtaining concordant results by both methods, provided the method was very closely adhered to, as outlined in our paper.

LABORATORIES OF PFISTER & VOGEL LEATHER COMPANY,
Milwaukee, Wis., June, 1918.

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DETERMINATION OF FREE SULPHURIC ACID IN LEATHER.*

By J. S. Rogers.

The Procter and Searle method for the determination of sulphuric acid in leather is being used to-day by many leather chemists, and although it is known to be subject to a number of errors, it is probably the best method that has yet been developed for this determination. It may be possible, after investigation, to make modifications which will eliminate some of the errors. The foundation for this investigation must be laid upon knowledge compiled from various experiments.

There has been very little collaborative work done with this method, and the knowledge now available is, therefore, meager. It is hoped that the work outlined this year may add some information of value.

Only slight modifications in the manipulation of the method have been proposed in the directions, but the work has been planned to determine:—

(*a*) How closely the results of different laboratories will agree.

(*b*) How the results obtained compare with theoretical results.

(*c*) How the results obtained using NaOH and phenolphthalein compare with those obtained when using Na_2CO_3 and methyl orange.

(*d*) How the presence of various materials will affect the results.

(*e*) How much loss of alkali (and consequent high acidity) will be obtained by too high a temperature of ignition.

(*f*) How the alkalinity of the ash may be expected to affect the results.

A sample of leather was prepared and sent out with the following directions to several members of the association:—

DIRECTIONS FOR COMMITTEE WORK ON THE DETERMINATION OF SULPHURIC ACID IN LEATHER.

A. L. C. A., 1918.

Transfer the sample to a larger covered container.

*Committee report presented at the Annual Meeting at Atlantic City, May 16, 1918.

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A. Ash 5 grams of the original leather in a platinum dish if available (if in porcelain, so state), over a gas flame of medium height or in an electric muffle at a dull red heat, and determine the per cent. ash.

To the ash residue add a measured excess of N/10 H_2SO_4, boil and titrate back with N/10 NaOH using phenolphthalein.

Report the per cent. of alkalinity thus found in terms of NaOH.

1. On 2 grams of the original leather determine the H_2SO_4 by the Procter and Searle method modified as follows:—

Add 25 cc. of N/10 Na_2CO_3 to the leather, mix thoroughly, place on steam bath, and allow to remain there over night. Burn off slowly (*a*) over a gas flame of medium height, or (*b*) in an electric muffle, raising the temperature slowly up to but not above dull redness. Continue this ignition until the leather is thoroughly charred and nearly all of the carbon is burned off. Cool the dish and wash down the sides with about 15 cc. of hot distilled water, break up any small lumps of charcoal, set on the steam bath and evaporate to dryness. When thoroughly dry, ignite again, heating gently at first to avoid decrepitation. When the residue is free from carbon, cool, add 25 cc. of N/10 H_2SO_4, set on the steam bath for 15 minutes, filter through a small filter, and wash thoroughly. Titrate with N/10 Na_2CO_3 using methyl orange. Calculate the per cent. acid.

2. Add to 2 grams of the original leather 0.06 gram of actual H_2SO_4 (add the required number of cc. of N/10 H_2SO_4). Then proceed exactly as directed under 1.

3. Add to 2 grams of the original leather 0.02 gram of any commercial sulphonated oil. Then proceed exactly as directed under 1.

4. Add to 2 grams of the original leather 0.04 gram of $Al_2(SO_4)_3$ dissolved in 5 cc. of water. Then proceed as directed under 1.

5. Add to 2 grams of the original leather 0.04 gram of $MgSO_4 \cdot 7H_2O$ dissolved in 5 cc. of water. Then proceed as directed under 1.

6. On 2 grams of the original leather determine the acidity as directed under 1, except that the N/10 Na_2CO_3 be replaced throughout by N/10 NaOH and the solution be boiled to remove

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CO_2 before the final titration. Use phenolphthalein as indicator.

7. Add to 2 grams of the original leather 0.06 gram of actual H_2SO_4, then proceed as directed under 6.

8. Add to 2 grams of the original leather 0.04 gram of $Al_2(SO_4)_3$ dissolved in 5 cc. of water. Then proceed as directed under 6.

9. On 2 grams of any commercial sulphite cellulose extract determine H_2SO_4 as directed under 6.

10. On 2 grams of any sulphited quebracho extract determine as directed under 6.

11. Evaporate 25 cc. of N/10 Na_2CO_3 solution, and ignite for half an hour at the highest temperature of the Bunsen burner. Take this residue up with 25 cc. of N/10 H_2SO_4. Then titrate with N/10 Na_2CO_3 if it is found that this solution reacts acid. Report the acid found in per cent. on the basis of a 2-gram sample of leather.

12. Repeat using N/10 NaOH instead of Na_2CO_3.

Make all the determinations called for in duplicate with the exception of those under A.

Test the reaction to methyl orange and phenolphthalein of the sulphonated oil and the aluminum sulphate used, and report the results obtained. If acid in reaction, state the number of cubic centimeters of N/10 alkali required for neutralization.

Results have been received from the following:

A. M. Caplan, Graton and Knight Mfg. Co. Laboratory.

J. B. Churchill, American Leather Research Laboratory.

R. W. Frey, Leather and Paper Laboratory, Bureau of Chemistry.

W. A. Fox, Elk Tanning Co. Laboratory.

D. Y. Yen, Pratt Institute.

G. W. Schultz, Elk Tanning Co. Laboratory.

Faust and Fortner, Yocum-Faust, Ltd.

F. F. Marshall, Kistler Leather Co. Laboratory.

These results are shown in Table I. In this table when results were reported in percentage alkalinity, they have been calculated to percentage minus acidity as H_2SO_4. This has been done to facilitate the comparison of results obtained upon the original leather with those obtained after the addition of acid or other materials.

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TABLE I.

No.	Description of sample	Caplan % H_2SO_4 found	Churchill % H_2SO_4 found	Frey % H_2SO_4 found	Fox % H_2SO_4 found	Faust and Fortner % H_2SO_4 found	Schultz % H_2SO_4 found	Marshall % H_2SO_4 found	Yen % H_2SO_4 found
1.	Original leather	0.14	−0.11	. .	−0.17	. .	−0.20	−0.07	−0.11
	Using Na_2O_3	−0.13	−0.12		−0.16	. .	−0.15	−0.03	−0.11
	Average	−0.14	−0.12	−0.22	−0.16		−0.18	−0.05	−0.11
2.	Original leather + 4 % H_2SO_4	2.72	2.77	2.72	2.72	. .	2.73	2.97	2.71
	Using Na_2CO_3	2.72	2.80	2.74	2.70	. .	2.73	2.92	2.81
	Average	2.72	2.78	2.73	2.71		2.73	2.95	2.76
3.	Original leather + 1 % sulphon'd oil	−0.10	−0.21	. .	−0.10	. .	−0.10	−0.07	−0.12
	Using Na_2CO_3	−0.11	−0.21	. .	−0.10	. .	−0.08	−0.07	−0.08
	Average	−0.11	−0.21	−0.16	0.10		−0.09	−0.07	−0.10
4.	Original leather + 2 % $Al_2(SO_4)_3$	0.17	0.69	0.23	0.61	. .	0.73	0.12	0.16
	Using Na_2CO_3	0.18	0.64	0.25		. .	0.83	0.12	0.13
	Average	0.18	0.67	0.24	0.61		0.78	0.12	0.15
5.	Original leather + 2 % $MgSO_4.7H_2O$	−0.12	0.18	. .	−0.07	. .	−0.08	−0.07	0.08
	Using Na_2CO_3	−0.10	0.18	. .	−0.05	. .	−0.05	−0.07	0.08
	Average	−0.11	0.18		−0.06		−0.07	−0.07	0.08
6.	Original leather	0.05	−0.08	. .	−0.05	0.61	Neutral	−0.07	Neutral
	Using NaOH	0.03	−0.08	. .	−0.07	0.73			
	Average	0.04	−0.08	−0.10	−0.06	0.67		−0.07	
7.	Original leather + 3 % H_2SO_4	2.93	2.77	2.86	2.72	3.72	2.70	2.94	2.73
	Using NaOH	3.05	2.77	2.80	2.74	3.62	2.65	2.99	2.78
	Average	2.99	2.77	2.80	2.73	3.67	2.68	2.97	2.76
8.	Original leather + 2 % $Al_2(SO_4)_3$	0.76	1.46	0.64	1.45	. .	1.44	0.85	0.69
	Using NaOH	0.73	1.44	0.65		. .	1.44	0.94	0.69
	Average	0.75	1.45	0.64	1.45		1.44	0.90	0.69
9.	Sulphite cellulose extract	2.15	6 samples	4.55	0.31	. .	0.92	−0.17	2.47
		1.85		4.61	0.31		0.27	−0.15	2.31
	Using NaOH	2.05	Range			. .			
		1.57	0.71-4.78			. .			
	Average	1.90		4.58	0.31		0.60	−0.16	2.40
10.	Sulphited quebracho extract	0.00	None	.	−0.06	. .	−0.12	−0.12	−0.07
	Using NaOH	0.00	9 samples	. .		.	−0.08	0.07	−0.11
	Average	0.05			−0.06		−0.10	−0.10	0.09
11.	Standard Na_2CO_3 solution	0.17	Bus'n Mk'r	0.52	0.29	. .	0.22	0.05	0.04
		0.13	0.06 0.20	0.50	0.17	. .	0.29	0.04	0.07
		0.13	0.06 0.22			. .			
		0.15				. .			
	Average	0.15	0.06 0.21	0.51	0.23		0.25	0.05	0.05
12.	Standard NaOH solution	0.20	None with	0.45	0.15	. .	1.48	0.07	0.00
		0.25	Bunsen	0.51	0.10	. .	1.70	0.00	0.02
		0.25				. .			
		0.26				. .			
	Average	0.21		0.48	0.07		1.59	0.07	0.01
A.	Percentage ash	0.47	0.50	0.47	0.46	0.54	0.53	0.49	0.48
	Alkalinity of ash (NaOH)	0.23	0.20	0.25	0.26	0.014	0.25	0.80	0.24

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COMMENTS.

A. M. CAPLAN: No. 9. Great difficulty was experienced in burning off the carbon from the sulphited cellulose extract used in this determination. It was found necessary to take up the ash with water three times in order to completely burn off the carbon. After titration a considerable quantity of $Fe(OH)_3$ was found to have been precipitated.

No. 11. In this determination a lesser loss of alkalinity was found when the dish was heated on the steam bath after adding 25 cc. of N/10 H_2SO_4 than when not heated in this manner. Thus, when heated, results expressed in per cents of acid on 2 grams of leather were: 0.17, 0.13, and 0.15 per cent. H_2SO_4, respectively; but when not heated they were: 0.26 and 0.34 per cent. H_2SO_4.

No. 12. The results when heated were: 0.20, 0.25, 0.24, and 0.25 per cent., respectively; and when not heated were: 0.37, 0.36 per cent. H_2SO_4.

The effect of varying the amount of Na_2CO_3 in the Procter and Searle method was investigated as far as time would allow, with the following results:

Volume N/10 Na_2CO_3 used cc.	H_2SO_4 found Per cent.
25.00	—0.20
25.00	—0.19
20.00	—0.20
20.00	—0.25
15.00	—0.21
15.00	—0.25

Similar tests were made on the modified Procter and Searle method, with the following results:

Volume N/10 Na_2CO_3 used cc.	H_2SO_4 found Per cent.
20.00	—0.23
20.00	—0.17
15.00	—0.24
15.00	—0.23

J. B. CHURCHILL: All determinations were done in platinum. The ignitions carried out over an ordinary Bunsen burner, evaporations and dryings made in Freas electric oven at 100° C.

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No. 3. Sulphonated oil was neutral to methyl orange, acid to phenolphthalein, and gave an acidity of 0.37 per cent. when run by the Procter-Searle method.

No. 4. The amount of aluminum sulphate used corresponds to 2 per cent. anhydrous salt.

No. 9. I have examined in this laboratory six samples of sulphite cellulose extracts by the Procter-Searle method obtaining the following results:

	Per cent.
No. 1	0.71–0.71
No. 2	1.99–2.08
No. 3	1.79–1.81
No. 4	3.65–3.67
No. 5	4.21–4.41
No. 6	4.64–4.78

No. 10. I have examined nine samples of sulphited quebracho extracts by the Procter-Searle method and in no case found acidity.

No. 11. The temperature of ignition was as high as I could get with both Meker and Bunsen burners, and were very much higher than obtained in any ignitions used in making the determinations. If carefully done at a temperature not exceeding that used in the determinations, I find that there is practically no loss of alkali in the ignition.

No. 12. These determinations were made over the Bunsen burner and not with the Meker burner.

R. W. FREY: It is interesting to note that the percentage of alkalinity plus the percentage acid under 2 or 6 gives practically the theoretical 3 per cent. acidity. I am inclined, however, to believe that this does not mean much. It seems to me that there could be an appreciable quantity of H_2SO_4 present in a leather, the ash of which is still alkaline, as for example from a leather containing Epsom salts, some of which on ashing would be likely to go to the oxide.

Phenolphthalein with NaOH gave a decidedly better end point in all the determinations. The end points were none too good with either indicator in the presence of $Al_2(SO_4)_3$, and were particularly poor with methyl orange. (In No. 4, 2 per cent. $Al_2(SO_4)_3 \cdot 18H_2O$ was used.)

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The oil used for No. 3 is styled a sulphonated nutricod and contains 0.48 per cent. N obtained by distilling with MgO. A qualitative test showed the presence of sulphur in decided quantity. (In No. 3, 2 per cent. sulphonated oil was used instead of 1 per cent.)

The sulphite cellulose extract contained an appreciable quantity of aluminum.

The ignitions under 11 and 12 were made in platinum and a very high temperature was obtained, much higher than one would intentionally get in making an ash or a Procter-Searle determination.

It is rather difficult to draw any conclusions from these meager results, but the indications are that there is little choice between the two indicators. I believe, however, that NaOH and phenolphthalein will consistently give higher acidity.

W. K. ALSOP: It is our opinion that the Procter and Searle method is superior to either of the modifications you give. One reason for this is the fact that an excess of acid is in contact with the water insoluble ash, a part of which, at least, it is essential shall be acted on by the acid if correct results are to be obtained. This applies particularly in case of the presence of such a substance as $Al_2(SO_4)_3$. Another is that the soluble sulphates are washed out and are not subject to the longer heating in the presence of charcoal. The charcoal can also be more readily burnt after washing. The matter of loss by decrepitation by this method you give is to be considered.

It is also our belief that the Procter-Searle method as we understand it is ordinarily carried out can be improved. Also that each detail in reference to procedure be studied and the manner in which it is to be done specified, as it is apparent from our tests that what may seem perhaps rather unimportant variations in procedure may make considerable difference in results.

The effect of heating on steam bath or boiling the standard acid after addition to the ash is indicated by results in Table II and further experiments on another sample of leather are shown in Table III.

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TABLE II.—COMMITTEE WORK—SULPHURIC ACID IN LEATHER—G. W. SCHULTZ, 1918

Leather from J. S. Rogers. Proctor & Searle method modified.	Original Leather	Leather + *2 per cent. $Al_2(SO_4)_3$	Another sample of leather			
Ash obtained after burning; filter and charcoal is boiled with the N/10 H_2SO_4 for a few minutes.	— 0.25 per cent.	— 0.12 — 0.12	Rogers No. 1	Rogers No. 1	Rogers No. 1 except 35 cc. N/10 H_2SO_4 used.	Procter & Searle method except heated on steam bath for 15″ after adding acid.
Ditto, except 15 cc. Na_2CO_3 and 25 cc. H_2SO_4 used.		— 0.18	Leather	— 0.20 + 0.18 + 0.15	+ 0.12 + 0.10 + 0.07	+ 0.07 + 0.04 0.00
Ditto, except 15 cc. Na_2CO_3 and 15 cc. H_2SO_4 used.		— 0.12	Ditto — 2 per cent. $Al_2(SO_4)_3$	+ 0.81 + 0.84 + 0.86	+ 0.40 + 0.43 + 0.45	+ 0.35 + 0.34 + 0.33
Instead of boiling ash with H_2SO_4 it was heated 15″ on steam bath.		+ 0.29 + 0.25				

* Acidity—0.10 per cent. on 2 grams leather

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TABLE III. - EXPERIMENTS WITH PROCTER-SEARLE METHOD—G. W. SCHULTZ, 1918

	1	2	3	4	5	6
	Procter & Searle method as given L. L. L. B. page 309 Per cent. H_2SO_4	Same as 1, but using N/10 H_2SO_4 Per cent. H_2SO_4	Same as 2, but letting ash stand in contact with N/10 H_2SO_4 one hour at room temperature Per cent. H_2SO_4	Same as 2, but heating ash with N/10 H_2SO_4 on steam bath for 15 minutes Per cent. H_2SO_4	Same as 2, but boiling ash with N/10 H_2SO_4 Per cent. H_2SO_4	J. S. Rogers modification as used in committee work Per cent. H_2SO_4
A. Original sample	0.05	0.07	0.03	−0.07	−0.05	0.29
B. Original sample + 3% $MgSO_4.7H_2O$	0.15	0.15	0.30 0.37	−0.07	−0.05	0.74
C. Original sample + 6% $MgSO_4.7H_2O$	0.37	0.56	0.44	0.10	−0.05	0.98
D. Original sample + 3% $MgSO_4.7H_2O$. + 1% H_2SO_4	1.27	1.27	1.13	1.01	0.98	1.71
E. Original sample + 2% $Al_2(SO_4)_3$	0.25	0.34	0.25	−0.07	−0.03	0.71

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The results in Table III are interesting. They show the effect of heating the ignited residue with the standard acid in the presence of and in the absence of magnesium sulphate. The results shown in columns 4 and 5 of Table III are good and these procedures should be further investigated. The results in column 6 are of an entirely different nature from those obtained by the committee, following the same procedure, using the sample of leather sent out.

Mr. Schultz suggests that the method should be used as follows:

Two grams of leather treated with 25 cc. of N/10 Na_2CO_3 and evaporated to dryness, charred carefully (with the smallest possible flame). About 25 cc. of hot water added and large lumps of charcoal are broken up, then brought to a boil and boiled for about one minute, filter and wash dish and filter well with hot water, collecting filtrate in a 250 cc. beaker. Incinerate filter in the original dish, cool and add 25 cc. N/10 H_2SO_4 and bring to a boil and boil for a few minutes. Wash the dish into the beaker containing the first filtrate (through a filter paper if necessary). Titrate the contents of the beaker using methyl orange as indicator. Cover glass should be used when boiling in the dish.

J. M. SELTZER: We believe that the Procter-Searle method using sodium carbonate and methyl orange for titration gives reliable results as far as the work done in this report goes, including the chemicals used in these experiments.

It will be noted, however, that when sodium hydrate and phenolphthalein are used, a slight difference results in the percentages due to the fact that the aluminum sulphate is acid to phenolphthalein, but very nearly neutral to methyl orange. The sodium hydrate with phenolphthalein indicator gives a very clear end point, but the phenolphthalein is very much more sensitive to certain chemicals than is the methyl orange, and for this reason we believe it better to use the methyl orange indicator.

SUMMARY.

(*a*) *Agreement of Results.*—With a few exceptions, the results obtained by different collaborators agree reasonably well in the experiments on the original leather alone, and on the original

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leather to which were added H_2SO_4, sulphonated oil, and $MgSO_4 \cdot 7H_2O$, respectively. The variations observed in the results in the experiments where $Al_2(SO_4)_3$ was used may be due to the fact that different amounts of water of crystallization were present in the aluminum sulphate, or to different end points obtained with different indicators, or to difficulty in dissolving the ignited aluminum compounds in dilute H_2SO_4. The percentage of apparent acidity thus found gives some idea of the errors introduced by the presence of aluminum sulphate.

The results on sulphite cellulose extract alone vary considerably in different samples, while those obtained on sulphited quebracho extracts run quite uniformly.

The loss of alkali on ignition is considerable at high temperatures and apparently varies with the conditions of ignition.

(*b*) *Comparison of the Results Obtained with the Theoretical.*—If the results obtained in the cases where H_2SO_4 was added are compared with the amount of acid added they are found in all cases except one to be low. If, however, corrections are made for the alkalinity of the leather as found by the Procter and Searle method, the following corrected percentages will be obtained:

Using Na_2CO_3

2.86, 2.90, 2.95, 2.87, 2.91, 3.00, and 2.87 per cent., respectively.
Average, 2.91 per cent.

Using NaOH

2.95, 2.85, 2.90, 2.79, 3.00, 2.68, 3.04, and 2.76 per cent., respectively.
Average, 2.87 per cent.

Now if the alkalinity of the ash be calculated in terms of minus per cent. acidity as H_2SO_4 and this value be used to correct the results obtained in the experiments when the H_2SO_4 was added, the following results will be obtained:

Using Na_2CO_3

3.00, 3.03, 3.04, 3.03, 3.04, 3.75,* and 3.05 per cent., respectively.
Average, 3.03 per cent.

Using NaOH

3.27, 3.02, 3.11, 3.05, 2.99, 3.77,* and 3.05 per cent., respectively.
Average, 3.08 per cent.

(*c*) *Comparison of Results Using Na_2CO_3 and NaOH.*—By comparing the result obtained when using NaOH and phenolphtha-

* Omitted from average.

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lein with those obtained with Na_2CO_3 and methyl orange, it is found that on the original leather the acidity (*e. g.*, lack of alkalinity) is greater when NaOH is used. On the sample containing the acid there is not much difference. And when the corrections for the blank on the original leather are applied the results with the two alkalies agree quite closely. There is, however, a decided difference on the samples which contain $Al_2(SO_4)_3$, the NaOH giving much more acid than the Na_2CO_3.

(*d*) *Percentage Acidity as Affected by Some Materials.*—The sulphonated oils used in these experiments apparently did not materially affect the percentage of acidity. This is somewhat surprising since some oils of this type have been known to show over 2 per cent. acidity by the Procter and Searle method.

Results indicate that the presence of sulphite cellulose extract will tend to increase the percentage of acid shown by this method. The amount of this increase varies considerably with the different samples.

Sulphite quebracho extract apparently produces little effect.

(*e*) *Result of Excessive Ignition.*—If too high temperatures are employed alkali will be lost and there will result an apparently high acidity.

(*f*) *Effect of Ash Alkalinity Upon the Results.*—The alkalinity of the ash will doubtless have its effect upon the acidity value obtained. Let us consider four cases.

First, a leather which is neutral, if analyzed by the Procter and Searle method should show a neutral reaction at the end of the determination, provided there is no free alkali present from the ash. If, however, the latter is alkaline the final reaction will be alkaline by an amount equal to the alkalinity of the ash.

In the second case suppose a leather to be decidedly acid in reaction but giving an alkaline ash. Such a leather analyzed by the Procter and Searle method would probably show an acidity, but this would be less than the true acidity by an amount equal to the alkalinity of the ash. Leather Nos. 2 and 7 might be placed in this class.

In the third case consider a leather which is very slightly acid and which gives an ash with more than sufficient alkali to neutralize the free acid. Analysis by the Procter and Searle method of this leather would indicate alkaline leather. But the alkalinity

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thus obtained would be less than that shown by the ash, by an amount equal to the free acid originally present. The leather in Nos. 1 and 6 might be placed in this class.

The fourth case is the one in which the leather is alkaline in reaction. The Procter and Searle method should show an alkaline reaction practically equal to the alkalinity of the ash.

Recommendations.

I. It is recommended that a detailed study of the procedure of the Procter and Searle method be made.

II. That further study be conducted to determine the proper amount of alkali to use.

III. That the effect of the alkalinity of the ash upon the acidity found be further investigated.

IV. That methods be developed for determining and correcting for materials such as Fe, Al, and NH_3 compounds.

V. That any new methods giving promise of better results be reported.

Discussion.

Mr. Churchill: I feel that the method as carried out would probably be accurate for an unloaded leather, but I am in doubt as to what confidence we could place in the results of the determinations when run on leathers highly loaded with magnesium sulphate. With highly loaded leather the chance is that any variation of the method would be more likely to cause a variation in the result obtained. The presence of the sulphates of iron, aluminum and chromium will all tend to increase the acidity above its true value.

From the work I have done I believe that the method as outlined by Mr. Rogers compares favorably with the original Procter and Searle method. A leather which showed an original acidity of 0.26 per cent. by either method gave identical results by both methods after 2 per cent. of sulphuric acid had been added to the sample.

I think the filtration method is, under ordinary circumstances, the more rapid, as it allows the burning of the residual carbon with the filter without the necessity of drying. In Mr. Roger's method there is great danger of loss of sodium carbonate by decrepitation when starting the ignition of the evaporated and sup-

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posedly dry residue. This danger is entirely avoided in the filtration method. The use of different amounts of sodium carbonate seem to give slight variations in the results with leathers having a low acidity. The results of several determinations using 25 cc. of sodium carbonate were all between 0.24-0.26 per cent. The results obtained on the same leather were between 0.35-0.37 per cent. when 50 cc. of sodium carbonate were used. With 2 per cent. of sulphuric acid added to this leather the use of 25 cc. or 50 cc. of sodium carbonate seemed to make but little difference, 2.25 per cent. being found in each case.

In the determination of the acidity of sulphite-cellulose by the Procter-Searle method the use of different amounts of sodium carbonate gives widely varying results; determinations run with 50 cc. giving nearly twice the acidity as compared with those run with 25 cc. I have no explanation to offer unless it is that the leather or substance under examination contains organically combined sulphur that is held back by an excess of sodium carbonate and oxidized to sodium sulphate. As it seems more than likely that varying results may be obtained by variations in the detail of the method, it would be my suggestion that a very definite procedure be adopted and strictly adhered to if this method is to be used.

There is another point about which I should like to ask. That is the use of porcelain instead of platinum. It seemed impossible to get check results when porcelain was used. Possibly the quality of the porcelain is at fault. After one or two determinations the glaze is entirely removed. I have only tried out Japanese porcelain.

I ran a large number of these determinations in both porcelain and platinum. The results of those made in porcelain would not check with themselves and were in all cases from 30-50 per cent. higher than those made in platinum.

MR. OBERFELL: I have used platinum and porcelain on this work, and I never noticed any difference in the results, but I lose half the determinations by the porcelain cracking. I very seldom find the porcelain will stand up under the method. I also find that the Royal Berlin porcelain will lose its glaze the same as Japanese or any of our American porcelains. I have never noticed that it affected the results any.

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MR. ROGERS: I did some work at the Bureau of Chemistry comparing the use of porcelain and platinum. I also made some determinations in silica, and I didn't find at that time any marked difference, but I think that I was using the Berlin porcelain. I concluded from those experiments it would be perfectly safe to use porcelain in place of platinum.

One point I wanted to lay special emphasis upon, and that is this: I don't believe that enough attention has been given so far to the effects of the alkalinity of the ash in this determination. I think this ought to be studied very carefully in the work that goes out next year. If we compare the results obtained, we find that the alkalinity has a very decided effect; that is, an eighth to a quarter of a per cent., which is enough to make quite a difference. The results that we obtained this year certainly indicate that if a correction for the alkalinity of the ash be made, that in practically all the cases of the unloaded leathers, nearly the theoretical acidity will be obtained.

In the presence of a substance like aluminum sulphate, I believe the alkalinity of the ash could still be considered; I do not believe with dilute acid like N/10 sulphuric acid that all of the aluminum will go into solution, and if not, the results for acidity will be high.

MR. FAUST: I hardly know whether I am qualified to speak very much on this subject, as we were not able to do a great deal of work with this committee, but from what little work we did, I believe that the Procter-Searle method is better than has been commonly supposed.

As I understand the report, the principle materials which affect the accuracy of the results are aluminum, iron and ammonium compounds, and, to a lesser extent, sulphonated oil. So far as the aluminum and iron are concerned. I would hardly consider it, and as far as I can see, we are trying to evolve a leather here which will rarely be met with in practice. I think the Procter and Searle method, as modified, in probably nineteen cases out of twenty, is going to give quite accurate results.

MR. FOX: There are some sulphite cellulose extracts that contain aluminum in some form, probably aluminates.

On ashing these widely different results can be obtained depend-

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ing on the way it is burned. Tanners using such an extract introduce aluminum into their leather.

MR. ALSOP: If you find an ash alkaline from the leather, won't sulphuric acid be neutralized by the salts which produce the alkaline ash, and therefore you will find less sulphuric acid in the leather than was added?

MR. ROGERS: That might be true in same cases, and if so a leather containing such salts, when treated with a known amount of sulphuric acid would show upon analysis, less acid than was added.

I believe that it is possible to have a leather which is acid in reaction, but which will show an alkaline ash.

The hide substance and tanned hide substance have a great affinity for acids, and I would not be surprised if that acid might be held there mechanically without reacting with the neutral salts. In the Procter and Searle procedure, you add alkali, and it takes care of the acid, and at the end of the ignition you have a higher alkalinity, depending on the amount of carbonates and other materials yielding alkalies which are present.

MR. ALSOP: The best way to compare samples would be to take a sample of the leather, with no sulphuric acid in it, add a small amount of acid to take care of the alkalinity and make the determination according to the method, then add a definite amount of acid and make the determination again.

I think the acidity that is found in sulphite-cellulose extracts depends on the preliminary treatment of the sulphite-cellulose liquors. We have tested many samples of one brand and found them all alkaline by this method.

DETERMINATION OF LACTIC ANHYDRIDES IN LACTIC ACID.*

By F. C. Thompson and Kyohei Suzuki.

Free lactic acid is usually determined by rapidly tirating the diluted sample with standard alkali, using phenolphthalein as indicator, and taking the first full pink coloration as the end point.

* *J. S. L. T. C.*, April, 1918.

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This we shall refer to as the first titration. To determine remaining anhydrides (including lactide) two methods have been used, in each of which the remaining anhydrides are allowed to react with excess of alkali, the amount used being determined by titrating back. In one method[1] the excess of alkali is boiled for a short time with the anhydride, while in the second process the reaction is allowed to take place while standing in the cold for ten or fifteen minutes[2] As to the merits of the two methods there has been some controversy. The advocates of the first have claimed that the remaining anhydrides do not react completely with alkali in the cold, since the boiling method gives the higher results. Besson, however, showed that this difference between the two methods does not occur in the analysis of pure lactic acid, but only with commercial material, and he therefore urged that the extra consumption of alkali in this latter case must be due to impurities originating in sugar. Additional support to Besson's view is afforded by the odor and yellow coloration developed during the boiling process. It thus seems fairly certain that lactic anhydrides react completely in the cold with alkali in a moderately short time, and that consequently they are efficient deliming agents. Besson indeed found that lime-water could be used instead of sodium hydroxide for the estimation of anhydrides under exactly similar conditions. If, however, the cold reaction method is used (with any caustic alkali) there is always some absorption of atmospheric carbon dioxide, which, since phenolphthalein is used as indicator, affects the result according to the excess of alkali used and the time of standing. This difficulty is overcome by bringing the solution to a boil after the addition of a known excess of sulphuric acid and finally titrating with alkali.

It is advisable to state at this point that three anhydrides of lactic acid are known:

Lactolactic or lactylic acid, or lactic anhydride $CH_3CHOH.CO_2CH.CH_3COOH$

[1] Procter's *Laboratory Book*, 1918.

[2] Besson, *Collegium*, 1910, p. 73; Balderston, this JOURNAL, 1915, pp. 45 and 242.

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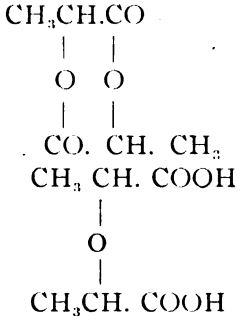
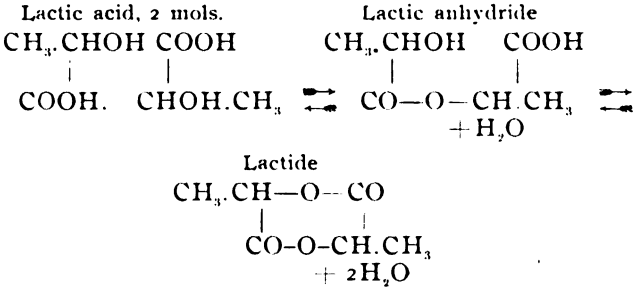
Lactide



and dilactic acid.

The first is a light yellow, amorphous body, easily soluble in alcohol and ether, sparingly soluble in water, and formed by heating lactic acid to 130°-140° C., though its preparation in the pure state is difficult if not impracticable. According to the reference books, lactic anhydride reacts at once with alkali to form lactate, and thus may be presumed to be included in the first titration in lactic acid analysis. Lactide is easily though slowly prepared by the distillation of lactic acid *in vacuo*. It is a well defined body, easily crystallized from ether and chloroform, very slightly soluble in water, and melts at 124°-125° C. Lactide reacts with alkali but not immediately. Part of the object of this paper is to give information on this point. Dilactic acid apparently does not occur in commercial lactic acid. The chemical relations of lactic acid, lactic anhydride and lactide are shown in the scheme given below. It is not known to what extent lactic anhydride is present in samples of ordinary lactic acid.



It is the object of this paper to support Besson's contentions by giving an account of some experiments with pure lactide, and also to maintain that the separate determination of lactide is

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wholly unnecessary and indeed delusive when the acid is intended for deliming. A study of lactic anhydride would have been of considerable interest, but this substance, as was stated above, is difficult to prepare in the pure state. However, it occupies, in point of constitution, a middle position between lactic acid and lactide, and reacts with alkali with greater ease than does lactide. Experiments showed conclusively that lactide reacts completely with alkali in the cold in ten to twenty minutes, according to the excess of alkali used. When, however, lactide was added to previously analyzed B. P. lactic acid, the lactide found in the mixture was very much less than the sum of lactide added and lactide previously present. This loss was more marked, the greater the quantity of lactide added. The first titration showed an increase exactly equivalent to the loss of lactide. It thus appears that in solutions containing acid and anhydrides, an equilibrium is ultimately reached which depends on the concentrations of acid, anhydrides and water, and probably on temperature also, a sufficiently complicated phenomenon. Lactide itself, on standing a few minutes with water is partly transformed into acid. These results led us to expect that analyses of any one sample of lactic acid would differ according to the dilution used, and experiments were made to test this point. It was found that if the titrations were done immediately after dilution no considerable error was introduced, but that very considerable discrepancies arose if the solutions were allowed to stand two hours before titration. Now this shows that results for lactide content are useless to leather manufacturers. Lactic acid. when used for deliming or other purposes is always in very dilute solution and stands for hours and even days. Obviously the amount of lactide present under such conditions is very different from that revealed by analysis of the original concentrated material. Since lactide reacts completely with lime in a short time, and is thus an efficient deliming agent, it seems to us that in the analysis of lactic acid, all that is needed is the determination of the sum of free acid, lactide and anhydride, which can easily be determined by allowing the sample to stand with excess of alkali for fifteen minutes, bringing to the boil with a known excess of standard sulphuric acid and titrating to phenolphthalein with caustic alkali. Of course, free sulphuric and volatile acids will be included in the

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result, and it may be necessary to determine iron, but two determinations will be replaced by one.

Experimental.

Preparation of Lactide. Lactic acid (B. P.) was heated for several hours at 100°-110° C., and then distilled *in vacuo* at about 135° C. White crystals of lactide were formed in the condenser and receiver. The yield was not very good. The crystals were well washed with distilled water (in which lactide is only very sparingly soluble), dried and recrystallized from ether or chloroform, washed again with water, then with a little ether, and finally dried in the steam oven or in the vacuum desiccator. The purified product consisted of white needles, and melted sharply at 124-124.5° C.

The purity of the lactide was shown by its melting point, and was also verified by titration. Definite quantities were dissolved in a little alcohol and ether, boiled for twenty minutes with a slight excess of sodium hydroxide, and the solution titrated back with acid, using phenolphthalein. The results were as follows:

	Lactide used Gram	Lactide found Gram	Percentage found
1	0.4770	0.4789	100.5
2	0.5000	0.5015	100.3
3	0.4120	0.4125	100.1

Lactide was also dissolved in pure ether and added to previously analyzed lactic acid. The quantity taken was equal to the quantity found a result very different from that obtained when the mixture was diluted with water.

	Lactic acid as solvent Gram	Lactide used Gram	Lactide found Gram	Percentage found
1	0.5320	0.0503	0.0505	100.4
2	0.5164	0.0406	0.0407	100.3

Reaction of Lactide with Sodium Hydroxide.—Small quantities of lactide were dissolved in 5 cc. of a mixture of equal parts of alcohol and ether, and an excess of decinormal alkali, 1.1 times the equivalent of the lactide, was then added to the solution. Titrations were made after the solutions had stood some minutes.

	Time of standing	Per cent. lactide reacted
1	5 min.	96.10
2	10 min.	99.05
3	15 min.	99.80
4	20 min.	100.30

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The lactide reacted completely in twenty minutes. A further experiment similar to the above was performed, in which an amount of alkali equal to twice the equivalent of the lactide was used.

	Time of standing	Per cent. lactide reacted
1	5 min.	100.05
2	10 min.	100.15
3	15 min.	100.30

The amount of lactide used was so small (about 0.05 gram) that the difference between 100.15 per cent. and 100.30 per cent. may be neglected, and the action regarded as complete in ten minutes, with a sufficient excess of alkali. A further experiment showed the influence of heat; a quantity of alkali was used equal to 1.2 times the equivalent of the lactide, and the heating was done on the steam bath.

	Time of heating	Per cent lactide reacted
1	3 min.	100.05
2	5 min.	100.10

Reaction of Lactide and Calcium Hydroxide.—Lactide was dissolved in ether and alcohol and allowed to stand in the cold with excess of lime-water. The titration was done by Besson's method. The results were precisely the same as with sodium hydroxide. If the alkali used was one and one-tenth times the equivalent of the lactide present, the reaction was complete in twenty minutes; if, however, the alkali was twice the equivalent of the lactide, five or ten minutes sufficed for the completion of the reaction.

Addition of Lactide to Lactic Acid.—In further experiments lactide was dissolved in ether, added to definite small quantities of analyzed lactic acid, diluted with 5 cc. of water, and the mixture analyzed. As the results show, there was a considerable loss of lactide in each case, and an equal increase in the lactic acid (first titration). It will also be seen from the figures that the differences are greater or less according to the amount of lactide added. This is no doubt due to the disturbance of an equilibrium by the addition of lactide and water. There is also a considerable dilution due to the water in the alkali used for titration.

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	A Lactide added %	B Lactide in original acid %	C Sum A + B %	D Lactide found %	E Difference C—D %	I. Free acid in orig'l sample %	II. Free acid after lactide added %	III. Difference II.—I. %
1	17.22	18.00	35.22	27.87	7.35	74.99	82.40	7.51
2	8.40	18.00	26.40	22.47	3.91	74.99	78.95	3.96
3	11.82	18.00	29.82	24.63	5.19	74.99	80.24	5.25
4	9.87	18.00	27.87	23.50	4.37	74.99	79.48	4.49
5	16.55	18.00	34.55	27.03	7.51	74.99	82.54	7.55

Action of Water on Lactide.—Lactide in small quantities (0.05 gram) was dissolved in 5 cc. portions of ether and alcohol mixture, and the solutions diluted with quantities of water. After standing five minutes, each solution was directly titrated with decinormal alkali, using phenolphthalein as indicator, in order to estimate the free acid developed. The results show a very considerable action of the water at ordinary temperatures. It must be remembered that further dilution is caused by titration.

	Water added cc.	N/10 alkali needed for free acid cc.	Percentage of transformed
1	0.3	0.83	11.9
2	2.0	1.07	15.4
3	5.0	1.43	20.5
4	10.0	1.55	22.3
5	15.0	1.92	27.6
6	25.0	2.50	36.0
7	100.0	3.60	51.8

The increase in dilution necessary to raise the amount of transformed lactide from 11.9 per cent. to 15.4 per cent. is about 200 per cent., *i. e.*, an increase of from 1 cc. to 3 cc. roughly, and this is in a solution containing originally no free lactic acid. Under these conditions the transformation of lactide should be most rapid. There is an increase in effect at greater dilutions. These experiments, in conjunction with the last series, raised the expectation that the analytical figures obtained for any sample of lactic acid would vary according to the dilution used for analysis, though not to such an extent as the figures of the last table, owing to the large amount of free lactic acid already present.

Analysis of Lactic Acid at Various Dilutions.—Experiments showed that unless dilutions vary very much and the solutions are allowed to stand some time between dilution and titration, no

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considerable errors are introduced. Nevertheless, for reasons adduced earlier in this paper, the separate determination of lactide in concentrated acid is of no use whatever to the leather manufacturer. The following results were obtained with samples of pure B. P. lactic acid. The figures in the second columns of the first two tables are the ratios of weight of water to weight of lactic acid used.

SAMPLE A.

	Time of standing Hours	Water added	Lactic acid Per cent.	Lactide Per cent.	Total Per cent.
1	3	4	75.90	15.12	91.02
2	3	40	76.43	14.60	91.03
3	3	100	76.70	14.22	90.02

SAMPLE B.

	Time of standing Hours	Water added	Lactic acid Per cent.	Lactide Per cent.	Total Per cent.
1	2	3	75.30	16.02	91.32
2	2	12	75.30	16.02	91.32
3	2	30	75.86	15.52	91.38

SAMPLE C.—Lactic acid diluted with thirteen times its weight of water.

	Immediate titration Per cent.	After two days Per cent.	Difference Per cent.
Lactic acid	75.93	76.83	0.90
Lactide	15.11	14.30	0.81

ABSTRACTS.

Nitrogenous Matter in Lime Liquors. A. TANNER. *La Halle aux Cuirs*, Feb. 17, 1918, p. 61. The opportunity arises often enough to defend the limes against unjustifiable accusations. Among the many misdeeds attributed to lime liquors is that of dissolving hide substance, with consequent loss in yield of leather. While it is admitted that the limes probably do attack the hide fiber to some extent, the tanner is apt to get a greatly exaggerated idea of the extent to which hide substance is dissolved because of the chemist's method of reporting his analysis. He will determine the nitrogen content of a liquor and calculate it all as hide substance, whereas in reality perhaps by far the greater portion of it was derived from the keratins of the epidermis and hair, and probably very little from the hide fiber which is convertible into leather. It is, therefore, not permissible to use the nitrogen content of a lime liquor as a measure of the loss of matter affecting the yield of leather.

J. A. W.

Upon the Synthetic Tannins. E. SCHELL. *La Halle aux Cuirs*, Dec.

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2, 1917, p. 394. (Abstract of communication to the French Association of Former Pupils of the Mulhausen Chemical School, which has recently been organized.) The exact composition of the simplest of our typical tannins, such as gallotannic acid from nut-galls, has not yet been determined, but great advances have been made in this direction. In recent years numerous tannin-like substances have been prepared such as digallic acid, diprotocatechuic acid, digalloyl-glucoses, and a whole series of bodies derived from the hydroxybenzoic acids. Particular mention should be made of the classical series of depsides obtained by combination of the chlorides of carbomethoxy- and carboethoxy-phenolcarbonic acids with the sodium salts of the various hydroxybenzoic acids. These syntheses, while very interesting from a purely scientific standpoint, have not found any technical application because of the difficulty of obtaining the requisite materials and the delicacy of the operations.

It is not, however, to the synthesis of true tannins that the author would call attention, but rather to the synthesis of bodies chemically very different from the tannins, but which have tanning properties and are commercially practical. Professor Meunier found that quinones and hydroquinones combine with hide substance forming products stable even in contact with boiling water which permit the consecutive absorption of vegetable tannins. This treatment with quinone gives an excellent preliminary tannage which avoids certain losses of hide substance, thus increasing the yield of leather.

An entirely new series of products appeared about 1912 under the name of the Neradols and consists of condensation products of a formaldehyde base with compound aromatic hydroxides or their derivatives soluble in water which contain, besides hydroxyl groups, one or more salt-forming acid groups. One example of this series is the condensation product of phenolsulphuric acid and formaldehyde. These bodies are capable of tanning hides, either alone or in conjunction with other tanning agents, and give a whole series of reactions characteristic of tanning materials, such as coloring iron salts a violet-blue and precipitating gelatin and basic colors.

It has now been found that neither formaldehyde nor hydroxyl groups are necessary to obtain products capable of tanning. Some of the various hydrocarbons under the action of sulphuric acid undergo condensation leading to soluble tanning products, which because of their simple and cheap technical production are certain to become of commercial importance. Organic chemistry will perhaps be called upon to play a rôle in the tannery analogous to that which it has played in the field of artificial colors. J. A. W.

Viscosity and Waxes. *Les Matières Grasses,* Jan. 15, 1918, p. 4858. According to Fabris an excellent means of examining waxes lies in measuring the viscosities of their solutions in nitrobenzene. Employing 10 per cent. solutions Fabris obtained the following values:

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Paraffin	3.49 to 6.69
Spermaceti	6.74 to 7.42
Tallow	8.31 to 8.50
Stearin	12.39 to 13.05
Beeswax	15.23 to 16.30
White wax	16.54 to 17.53
Japan wax	20.71 to 21.12
Carnauba wax	42.03 to 43.03

A wax adulterated with paraffin will give a low viscosity while one containing much Carnauba wax will give a high viscosity.

(The foregoing has evidently been taken from a paper by U. Fabris entitled, "Viscosity of Beeswax and its Adulterants," *Stazioni Sperimentali Agraria Italiane*, **48**, 595 (1915); *Chem. Abstr.*, **10**, 2411 (1916). Fabris recommends the use of Ostwald's viscosimeter. The determinations are carried on at 100° and referred to nitrobenzene as unity.)

J. A. W.

The Treatment of Anthrax with Normal Beef Serum. *N. Y. Medical Jour.*, April 13, 1918. Clarence H. Hyman and Timothy Leary (*Boston Medical and Surgical Jour.*, March 7) review the literature of the serum treatment of anthrax and report a case in which it was successfully employed. The modern conception of external anthrax is of a low grade infection, which usually remains localized for long periods, and tends to get well under expectant treatment, except in certain situations, such as the eyelid. Under any other treatment than that by serum if invasion of the blood stream occurs, the mortality is 100 per cent. Immune serum was formerly used, but was replaced by normal beef serum mainly through the activity of Kraus of Buenos Aires, who reported fifty cases treated with it with no deaths. In all 146 cases have been reported with one death. The most rational explanation of the activity of a normal beef serum in anthrax is that it obtains results by provoking a nonspecific proteid reaction. Foreign serum is, perhaps, the blandest agent which can be introduced into the body for the production of this reaction, and beef serum has the advantage over horse serum in that it does not give rise to serum sickness. Quoting from Kraus, they say that the results "exclude all doubt regarding the real and positive efficacy of this treatment in the cure of malignant pustule, and even of carbuncular septicemia. Hypodermic medication was sufficient in many cases, but in grave cases with intense symptoms, or accompanied by septicemia, the intravenous method is better and more sure and requires no more care than is necessary in other intravenous medication. Doses of 10, 20, or 30 cc. constitute the ordinary quantities of each injection, augmented to 40 and 50 cc. in more intense cases. It is interesting to note that the therapeutic application of heated normal beef serum has produced no general or local disturbances comparable to those frequently produced by horse serum. This last produces in 10 per cent. or more of the cases treated allergy, or serum sickness. Nothing comparable has appeared following

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the use of normal beef serum. In only two cases have we seen a slight hyperemic zone, with little intensity and fugitive, surrounding the point of injection, and found commonly following the injections, whatever the via employed, lead to an immediate elevation of the temperature with a descent in from 24 to 48 hours to the normal. At the same time there is produced a favorable local reaction, characterized by diminution of the edema and a bettering of the general condition. In some cases the edema progresses and the fever continues until a new injection is made.

Preparation of Tannic Acid, and Gallic Acid, and Pyrogallol. M. Mito. *Kogyo-Kwagaku-Zasshi (J. Chem. Ind.)*, Tokyo, 1917; *J. S. L. T. C.*, March, 1918. Tannin was extracted from Japanese gall nuts by four successive treatments, with water at 20° to 30° C., and the residue was pressed. In this way a 13 per cent. solution of tannin containing 82 per cent. of the theoretical quantity was obtained. Tannic acid was prepared by concentrating the extract to 20 per cent., extracting it with half its volume of ether and evaporating the ethereal extract. About 75 per cent. of the tannin in the aqueous extract was obtained. For the preparation of gallic acid the residual solution from the tannic acid preparation was concentrated to 20 per cent., and treated with 15 to 20 per cent. (by volume) of sulphuric acid (66° B., specific gravity 1.84) and the precipitated black mass was dissolved in water, decolorized with animal charcoal, and finally recrystallized from water. The yield was 62 per cent. of the tannin contained in the residual solution. Pyrogallol was prepared by heating the crude gallic acid with about three times its volume of water in an autoclave at 210° C. The crude product (yield, 63.5 per cent. of the gallic acid) was purified by crystallization from pure benzene.

Colorimetric Determination of Iron. E. R. Dovey. *Analyst*, 1918; *J. S. L. T. C.*, March, 1918. The following method obviates errors of comparison caused by differences in the concentration of thio-cyanate or in the general composition of the two liquids: A measured volume of the liquid under examination is treated with the thio-cyanate solution, and divided in the proportion of one-third and two-thirds between two Nessler cylinders. The standard iron solution is then added to the smaller portion until its color matches that of the larger.

Leather Preservation. Deputy Librarian, Worcester County Law Library, Mass., March 10, 1911; *J. S. L. T. C.*, March, 1918. Vaseline or similar high-grade preparation of this petroleum by-product is rubbed into the leather with the palm of the hand. The process has a tendency to slightly swell outward both the front and back covers, so the volumes are spaced out on shelves for several months until they can be closely ranked together again. Each volume should be rubbed three to five times according to the condition of the leather. The vaseline should be rubbed well into the grain of the leather and not merely dabbed on with a pad and left to dry in. The sides, back and edges are thus treated, care being

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taken not to get any on the paper. Small portions should be used and care taken to get more of the agent into the back and edges of the back than is rubbed into the sides. The treated volumes are placed on a drying shelf at least over night and then carefully examined and all surplus material rubbed into the dry parts of the leather. The process has been mainly employed on sheep bindings and should not require to be done again for at least ten years. It arrests decay, and leather thus treated has not the tendency to collect dust and dirt. The color of the leather is only slightly darkened. In some cases books may be vaselined, excess removed, and allowed to partially dry. They may then be given two coats of Zinsser's light colored book varnish reduced one-third with denatured alcohol.

Analysis of Commercial Dextrins. M. C. LAMB AND A. HARVEY. *J. Soc. Dyers and Col.*, 1918, 34, 10-11; *J. S. L. T. C.*, April, 1918. The following determinations are carried out: *Moisture.*—Five to six grams are dried at 100° C. in an air-oven for 4 hours. *Ash.*—The residue from the preceding determination is incinerated at as low a temperature as possible. *Water-soluble Matter.*—Ten grams are shaken with cold water, allowed to stand over night, an aliquot portion of the filtrate evaporated, and the residue dried. *Reducing Sugar.*—Determined in a portion of filtrate from preceding estimation, using Fehling's solution and calculating to dextrose (maltose is only present in dextrins manufactured by a diastase process, a method not frequently used commercially). *Starch.*—Free starch is tested for by the iodine reaction in the portion insoluble in cold water. The results of a number of analyses show that dextrins are liable to considerable variation in composition, and the following analytical standards for commercial dextrins are suggested: Moisture, 8-10 per cent.; ash, 0.1-0.3 per cent.; water-soluble matter, 75-85 per cent.; dextrose, up to 8 per cent. After allowing for any dextrose and soluble ash, the water-soluble matter may be taken to represent the dextrin. The sample should give a neutral reaction. The darker colored samples contain the highest proportion of water-soluble matter; very dark samples frequently contain a high proportion of dextrose; buff-colored dextrins are preferable to white samples, as they are not so likely to contain a large quantity of unconverted starch.

Critical Examination of Tanning Materials, Extracts, Chrome Liquors, and Leathers (*Continued*). R. LAUFFMANN. *Coll.*, 1917, 401-8; *J. S. L. T. C.*, May, 1918. *Estimation of Mineral Weighting Matter.*—Five grams of leather should be ashed at not too high a temperature to avoid volatilization of chlorides and melting of alkalies. An ash exceeding 1½ per cent. with vegetable tanned leathers, indicates weighting in which case the ash is treated with 10 per cent. HCl and warmed. If the ash dissolves, lead and barium are precipitated as sulphates. The solution is boiled with alcohol to reduce any chromate present, then made up to 250 cc. and 100 cc. of this is used for the ordinary method of gravimetric estimation of Cr, Al, Fe and Ca. If part of the ash does not dissolve it may con-

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sist of insoluble oxides or lead or barium sulphates. The insoluble portion is filtered off, dried, fused with sodium carbonate, treated with hot water and filtered. Any insoluble portion is treated with warm dilute acetic acid, filtered, and dilute sulphuric acid added to the filtrate. A white precipitate may consist of lead or barium sulphate which is filtered, dried and weighed. The filtrate is mixed with the soluble portion of the fused mass, after the latter has been acidified with HCl and also with the solution obtained on treating the leather ash with HCl. In these mixed solutions the Al, Cr and Fe are estimated as before, after the chromates have been reduced with alcohol. Having precipitated these bases the calcium and magnesium can be determined. To estimate alkalies a weighed quantity of the leather should be extracted with hot water, filtered, and sulphuric acid removed by adding excess of barium chloride. The filtrate should be evaporated to dryness with ammonium oxalate and ignited, taken up with water and the process repeated. The filtrate should be acidified with HCl, evaporated to dryness, residue carefully ignited and weighed as alkali chloride. The author concludes the chemical investigation of leather by giving details of the usual chromium estimation. The physical properties of the leather merit consideration. A brittle grain may be caused by

(1) excessive incorporation of filling materials or uncombined tannin,
(2) heat damaging the fibers,
(3) the use of too strong alkalies in liming,
(4) use of mineral acids in deliming, swelling, and bleaching.

Paessler's method of detecting free H_2SO_4 consists of putting 10 grams finely divided leather into a dialyzer which is suspended in pure water. The outer liquor is colored faint red with congo red solution. Leathers containing free acid impart a violet color to the dialyzed liquor, which may be due to either mineral or organic acids. If no sulphate ions are present in the dialyzed liquor free H_2SO_4 is absent. If they are present a further sample of the leather should be heated at a low temperature, preferably in vacuo, to expel all volatile acids. If the leather still shows an acid reaction on placing in the dialyzer then non-volatile organic acids (lactic and oxalic) should be tested for. If neither of these acids is present then the acid reaction must be due to sulphuric acid. There is no means of testing whether free H_2SO_4 is present or not if lactic and oxalic acids are present also. The quality of the leather depends to a large extent on the evenness and good penetration of the tannage, which can be tested by placing 1½-millimeter strips of leather in 30 per cent. acetic acid for 2 hours. Undertanned leather will swell up considerably and may show a transparent yellow portion through the middle tissue. The permeability of the leather to water can be ascertained by Kilp's method (*J. A. L. C. A.*, 1916). Nihoul proposes to measure it by the quantity of water forced through the leather in a certain definite time. Another method is that of Thuau and Korsak (*Coll.*, 1910, 229). The capacity of the leather for soaking up water can be determined by Nihoul's method. A piece of leather 25 square centimeters is weighed, dipped in

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water at 15° C. for half an hour, drained, weighed and laid 24 hours in water, drained and weighed again. The water absorbed should not exceed 35 per cent. in the half hour with butt pieces and 50 per cent. after 24 hours, or 40 per cent. after half an hour with offal leather and 55 per cent. in 24 hours. The author concludes with describing the boiling test for chrome leather, Fahrion's water resistance test (*Coll.*, 1908, 498), the determination of the tensile strength, and the specific gravity.

Quebracho Extract in Argentina and Paraguay. Commercial Attaché ROBERT S. BARRETT, *Commerce Reports*. The potential production of quebracho extract by the companies operating in Argentina and Paraguay is about 230,000 metric tons per annum, and in 1917 the actual production, nearly all of which was exported, amounted to 117,000 tons. The difference between the potential and actual productions, or 113,000 tons, could be produced and exported provided shipping was available and the various factories were able to secure a price for their product that would make their operations profitable.

Quebracho extract is produced by eighteen companies operating in Argentina and Paraguay. The most important of the quebracho extract producers is the Forestal Land, Timber & Railways Co., whose offices are located at Alsina, 269, Buenos Aires. This company, which has a capital of 15,000,000 gold pesos, is not only the largest producer of quebracho extract in the country, but also buys the product of other factories, which it sells in the United States and Europe. In 1916 and 1917 it had an agreement with practically all of the factories in the country for their production, and it is understood that this agreement was made with the approval of the British Government in order that exports of quebracho extract could be controlled and that the product might not be obtained by concerns in Germany and Austria. In 1917 the Forestal Co. exported 102,000 tons of extract out of the total of 117,000 tons that went from Argentina and Paraguay. The agreement was regarded as quite satisfactory by the producers, as during its existence the price of quebracho extract reached $190 United States currency per ton, as compared with the present price of $90. Some of the producers, however, were not satisfied with the arrangement and it was not renewed for 1918, with the result that there has been a great deal of competition, prices have fallen, and many of the factories have been compelled to discontinue operations. The lack of shipping has also caused a decline in exports, and for the first three months of 1918 the shipments reached only 20,000 tons. The manager of the Forestal Co. stated that there would be no question about Argentina and Paraguay being able to produce 200,000 tons of quebracho extract provided there was a market for this quantity.

The exportation of quebracho logs to the United States to be used for the manufacture of extract in that country in 1917 was 95,000 tons, which is equivalent to 25,000 to 30,000 tons of extract. If this extract was manufactured in Argentina or Paraguay and the importation of quebracho logs into the United States prohibited, it would save the transpor-

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tation of about 65,000 tons of logs per annum. It should be borne in mind, however, that a portion of these logs, probably 10 per cent., is shipped in obsolete sailing vessels, which are unavailable for the shipment of other products, and the remainder of the logs are also shipped in sailing vessels which, while they might be used for the transport of other products, could not be employed for carrying quebracho extract unless the latter were packed in barrels or drums. It is understood that the quebracho logs which are sent to the United States are used for the manufacture of liquid quebracho extract, and while this could be produced in the factories here without difficulty, containers are not available for its transportation to the United States.

Denmark Manufactures Tanning Bichromates. Commercial Agent NORMAN L. ANDERSON, *Commerce Reports.* To supply the shortage of tanning bichromates caused by the cessation of imports from Germany, three new plants have undertaken the manufacture of these materials in Denmark. The one at Roskilde is operated by the Jorgen Winther chrome-leather factory and uses a process invented by Iwan Clausen, one of the company's engineers. This Roskilde factory is now supplying practically the whole chrome-sulphate consumption of the Danish leather industry. A limited company, "Chromium," has been organized near Christiania for the exploitation of this same process, and a factory has also been built in Malmo by the Svenska Chromatfabriken. All three factories have been equipped by the Danish engineering firm of F. L. Smidth & Co. The chrome ore is obtained from Norway, where it is found in large quantities, especially in Romsdalen. It is one of the materials coming under the exchange-of-goods agreement between Norway and Denmark. (See *Commerce Reports* for Apr. 29, 1918.)

Method for MgO. W. P. ECKDAHL. *The Chemist Analyst.* A rapid method for the determination of magnesia at the same time conserving otherwise wasted quantities of ammonia.

Using the filtrate from lime separation with ammonium oxalate, the solution is cooled, and the microcosmic salt solution added, stirring vigorously after pouring into the sample a filtered solution containing 2½ grams sodium hydroxide.

If the usual amount of ammonium chloride is present as is required and accumulated from previous separations, enough ammonia is set free by the reaction with sodium hydroxide which likewise facilitates the precipitation of magnesium phosphate in about one hour, giving results well within permissible limits of error.

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NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The Fourth National Exposition of Chemical Industries will be held in the Grand Central Palace, New York, during the week of

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Sept. 23, 1918. This exposition will be the largest chemical exposition ever held. The main purpose is to show the development of chemical industries in the United States and Canada notably since July, 1914. An elaborate instructive program is being arranged.

UPPER LEATHER FOR ARMY SHOES.*

By Fred A. Vogel.

In taking up the subject of trench leathers, it might be well to roughly outline the development of the present trench shoe, or, as the general staff prefers to call it "field shoe," by going back to the Spanish-American war when the old-fashioned bark tanned cowhide shoe was used, which was just an ordinary heavy shoe and could be described perhaps most intelligently by the term "heavy work shoe." This refreshes one's memory as to what was used in the army at that time. From this shoe the general staff went to the so-called "Munsen Last Marching Shoe" with which everyone is familiar.

In 1914, after the outbreak of the war, the United Shoe Machinery Company had in Boston an exhibit of army shoes which showed all types of shoes used by every nation of the globe.

The first thing that impressed a visitor at this exhibit was the very light type of shoe that was used by the American army at that time. It immediately raised the question in my mind of whether we were not on the wrong track in shoeing our soldiers with this light type of lined shoe. It was also at that time the only shoe which was made out of chrome upper leather. It will be taking up valuable time to detail the utter uselessness of this shoe under present fighting conditions, which does not need any further elaboration.

The care of the foot in the modern army is one of the most vital points that experience has taught the officers now engaged in the tremendous struggle in France. The lined shoe demands necessarily a light leather because a heavy leather with a cotton lining would make a very bulky and uncomfortable shoe. The

* Read at the Atlantic City meeting of the A. L. C. A., May 17, 1918.

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light upper wets through very readily and everyone knows that the shoe which is lined with a cotton lining, when wet through, gets to be very uncomfortable, sticky and hard to dry out. The lining crawls and experience has taught us that the soldier will cut this lining where it bulges and the inevitable result is blistered feet.

Therefore, early in the war the General Staff decided to adopt the unlined flesh finished shoe. When one looks back upon the shoe exhibit just mentioned and realizes the difference that existed between our own shoes and the shoes of the armies of Europe, one can readily see that when this new style of marching and field shoe was adopted a tremendous step forward was made in shoeing our army. This shoe, however, had proven not entirely satisfactory. There are no criticisms to be made on the last or the wear of the shoe, such as it was made, except that it was not heavy enough and that it was made on the welt principle. It would have been a very difficult matter to have gone at once from the "Munson Marching Shoe" to our present metalic fastened field shoe known as No. 1324.

While many criticisms have been made on the footwear furnished the army, we do not believe that they are entirely fair because the psychology of footwear plays an important part in the development of the present shoe. The American people have been used to a good-looking, snappy and flexible shoe, and grave doubts arose in the minds of the Shoe Committee last year when the change was considered—whether the men would be comfortable in this new shoe and whether they would take to the flesh-out principle as against the usual snappier looking grain-out shoe to which they were accustomed all their lives. The mistakes that were made are, therefore, pardonable to a great degree. It has been proven that the welt pattern for campaign shoes is not desirable because of the repair question envolved, and also because the welt pattern shoe is not as waterproof as the metalic fastened shoe now designed. Moisture leaks very readily through the stitches, especially where the welting is not done carefully and where there is a great prevalence of what is termed in shoe manufacturing "grinning seams." This is a shoe manufacturing detail which I will not enlarge upon at this time, but the gravest fault which the first flesh-out shoe had was its being entirely too

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light for the strenuous wear which it was subjected to when our troops got to France.

The sole leather, what there was of it, was satisfactory, but I might add that there was not enough of it.

The uppers were cut from whole sides which were made, to a great extent, from very large hides. The specifications called for from 2 to 2.4 mm in the vamp and ran down in the quarters and foxings as low as 1.5 mm. The tanner, in order to produce these thicknesses in quantity was obliged to split these large hides excessively, producing an open and porous flesh surface. A great deal of discomfort was had by the soldiers because of the shoe wetting through very readily. Another objection to the leather was that in making it in sides it did not permit of sufficient stuffing to overcome to a degree this openness because the flanks would have become too greasy and therefore not usable. Perhaps it would have been better to have stuffed it to such a degree that the flanks had become unusable, for we would have removed one of the shoe manufacturing problems envolved in making these shoes out of sides. Shoe manufacturers have taught their cutters all their lives to cut leather close and it was naturally this that brought about the result of cutting in undesirable parts of the hide out of the flanks and necks into vital parts of the shoe which did not improve the tightness of the shoe nor its wearing quality. This upper leather was also exclusively made of chrome re-tan, as we all know.

Early in February General Pershing cabled a demand for bark tanned leather in the field shoe for the American army. This demand was, no doubt, the direct result of observation amongst the French and British troops, all of which are shod with shoes made out of bark-tanned upper leather. British experience has proven that a vegetable tannage, well made, gives the most satisfactory results in the uppers of these shoes.

The problem that confronted the quartermaster corps almost at once was "Where can we get sufficient bark tanned leather of desirable quality to produce shoes in quantity for our ever-increasing army?" The problem is a great one and has necessitated a great deal of shifting and changing on the part of the quartermaster corps to educate tanners to make leather such as is now demanded. We found at once that there was not sufficient

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bark leather to make all the shoes out of such leather and we immediately set about to develop a re-tan leather which would be more satisfactory than the old re-tan which had gone into the shoes during the past year. We have improved this re-tan by cropping and taking off all the soft and undesirable parts, by splitting it less and by stuffing the remainder much heavier with solid filling greases. In getting the chrome re-tan leather up in this way we have done away with the opportunity of cutting undesirable open leather into the shoe.

In further discussing the development of our present army shoe, we must remember and always bear in mind that we are considering a leather from the standpoint of flesh finish altogether and that the problem of the grain is not envolved. It is the desire of the war department, however, to have nothing but bark leather as they have found in practice on the other side that it is most satisfactory. Not all of the quartermaster corps agree on this, but personally I do. Vegetable leather, well tanned, is the tightest, closest fibred leather that can be made. Its very nature, the combination of tannic acid with the hide, is the only permanent combination that has been found. Vegetable-tanned leather is always leather. Chrome is not. Chrome leather can be reduced back to the raw hide. The chrome can be washed out. I am not a chemist and do not intend to enlarge on this point, but I am merely bringing out this fact because it will aid in bringing out the conclusions that I wish to make. In tanning vegetable leather, you are building from the ground up. You have a solid foundation and experience has proven that nothing will be tighter and better in the long run than such leather of good substance, well made. In the re-tan your foundation is one that can be reduced back to hide. You form a fiber that can again be brought back to a mass and when you re-tan with vegetable on top of this you merely spread that fiber with vegetable tans and non-tans and will have a more open and porous piece of leather. These conditions you aggravate by tanning it more fully in chrome than when you leave it practically raw. By this I mean the more you fix and swell your fiber with chromic oxide, the more the same will be distended with a vegetable re-tan. By leaving unfixed gelatin in the hide you have something for the vegetable tannins to absorb and tighten down. The kind of

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vegetable-tanning material used in re-tanning also makes a vast difference. By using hemlock or tannins of the catechol type instead of gambier or tanning materials of the pyrogol type, you secure better results because of the mellowness or opening tendency of the latter as against the solid-feeling tendency of the former.

I am sorry to admit that all these mistakes were made in making re-tan for the army shoes the past year. It was chromed too heavily. It was split too much. It was re-tanned very frequently in vegetable-tanning liquors which had a tendency of opening the fiber and finally it was not sufficiently stuffed. So in many ways the leather made was perhaps re-tan leather of the poorest quality. By changing this we can improve the same materially, and this we are now doing, and wherever chrome-re-tan leather is going into the new shoes we believe we are making a better shoe than what had previously been made.

On the vegetable-tanned leather none of these objections arise because it is a tannage in itself that tends to solidity and tightness.

Much poor, rapid-tanned leather has been produced in America in the past decade. Our desire is to make leather more along the old-fashioned lines of slow tannage and lay away leather. It is to be made out of a smaller hide, not split excessively and well stuffed. If you adhere to this principle, we need never be ashamed of any shoe that goes on our soldiers' feet when they are fighting your battles and mine, nor need we worry that anyone in the trenches will suffer because of any equipment that we have given them. It cannot be denied that vegetable leather in the shoe needs more care and attention than the re-tan. It hardens more readily and does not resist the heat as well. This is a problem for the line officers and our able Shoe Committee has already taken this up with the inspector general and better results are promised for the future in this respect.

The matter of care for the shoes is a vital one. The average American citizen has not been taught to care for footwear. Styles have changed rapidly and shoes have been worn to the limit—only to be thrown away, with no thought of repair. It will be no small task to instil into our men foot and shoe care, but our allied armies have made great progress in this direction and we must emulate them if we wish to be successful.

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Full chrome leather is used by the English in one style of shoe and has been successful. It is used grain out and is not heavily stuffed, but embossed. It is a leather developed on the principle before mentioned of not over-tanning in chrome and allowing it to tighten down in the drying after fat liquoring, which is very scant, and then embossing it heavily, after the stock was tacked out, thus giving the tightest possible leather. The shoe made from this leather has been very waterproof, but also very air-proof, and, therefore, hot on the foot in certain weather conditions and not liked by the Tommies as well as shoes made from the bark and vegetable-tanned leather.

In conclusion, I can only state that our program just at present is to get away from the chrome re-tan entirely and go to the vegetable leather for the uppers for the metallic fastened shoe. We want 4,000,000 feet for September and 4,000,000 feet for October delivery and the Government has pledged itself to use this leather so ordered. We hope that the tanners will be able to furnish the quantities and furnish it right, so that we need not be ashamed of our future product, which, if satisfactory, will go a long ways to contributing to the success of the armies.

AN ADDRESS.*

By Major Kenneth D. Marlatt,
British and Canadian Recruiting Mission, Boston, Mass.

Gentlemen it is a great pleasure to be back again with some of my old friends. It is so long since I have been connected with the leather game and the leather chemist's game, that I am completely out of touch with any of the details of them.

However, there are one or two things before I speak of France at all that I should like to touch on. First of all, though I have been away all this time, I am more convinced now than when I went into this war of the absolute necessity of research work in this country along all lines, and I think we very greatly underestimate the value of it, and you will find the big men in this country, the men whose names are going to be remembered, are the men who will take the point of view that research is not car-

* Delivered at the Atlantic City meeting of the A. L. C. A., May 17, 1918.

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ried to the point it should be. We have a big job on after this war is over, and it is only through the benefits of research that we shall be able to compete with certain other nations.

The second is in connection with the army boots. I was very much interested in Mr. Vogel's paper, and I absolutely agree with everything contained in it. I had a good deal of experience in France, watching boots and conditions and I am very glad that the United States came to what is the practical boot so quickly. I am sorry to say we did not in Canada. We messed around for years before we came to it. I came direct from the chief boot inspector in England last year and took the matter up in Canada. I was told that the Canadian boot looked nice and was pretty and comfortable and that the men liked a pretty boot and all that rot which was natural at the start. But I agree with Mr. Vogel that we have passed that phase. Now the truth is that when our soldiers went from Canada to England they were not allowed to go to France with a Canadian boot. The Canadian boot was taken away and the regular British army boot issued and if they did happen to get to France with Canadian boots they were paraded there and the boots were taken away and the British army boot issued for the simple reason that our first boot was impractical, but even the improved boot was not thoroughly satisfactory.

One great advantage of having the flesh side out is that it is much easier to work in grease or "Dubbin" than through the grain. The men have to take care of their own boots over there and as they harden with all the wetting and drying out and mud, men are not going to do what they consider wasting time trying to work "Dubbin" through the grain side. This is the practical side of the question.

It might interest you to know a little about the question of feet. Over there in the trenches the officer commanding each platoon is held absolutely responsible for the condition of his men's feet and he must inspect the feet (I don't say they do—I know jolly well they don't, but they are supposed to). A man is required to take his boots and socks off to rub his feet with whale oil, or if he has no oil, to rub them anyway, and if a man gets trench-foot now in a part of the line where they don't think it is reasonable he is court-martialled and his officer is court-martial-

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led. As it is a court-martial offence to have trench-feet, it is a pretty serious proposition.

I happen to be at present in charge of the recruiting mission in Massachusetts, and I would like to speak to you all on the question of men. I don't know, perhaps I have a bug on the question, but there is only one thing that is going to win the war and that is men. All the other things are secondary—absolutely completely secondary.

The proof of it is this little example. Take any part of the front you want. Take a mile on that front. You can remove every aeroplane from that front for six hours and the infantry will suffer a great deal, but the chances are they will hold the line. You can remove all the guns, and the infantry will again suffer and suffer very severely, but the chances are again that they may be able to hold out, but remove the infantry from your front line for six hours and the whole line crumbles up. That is why we are working so hard to get men. There are lots of eligible British subjects we are working to get because we understand the need. When I tell you that in a year and a half in France our battalion was only up to strength twice, you realize the strain placed on the men when reinforcements are not sent. Twice only in a year and a half our battalion was up to strength.

Now for example, on the Somme on the 15th of September, when there should have been at least 850 in attack, if we had had a full battalion, there were a little over 700. That was good and we considered that practically up to strength. On the first of October when they attacked again, we took half of the quartermaster's stores men. The quartermaster stores and transport men are attached to each battalion, not to a regiment. They took half of our quartermaster's stores men and half of our transport men and then made up a total strength of 450 to go in and do the attacking. Well, that is men. And then they wonder why the German comes through as he does. Men can,—do go in and make an attack like that, fight great odds and hold for a short time, but it is not humanly possible for the same men to endure continued assaults from men who are brought on fresh for periods running for five, seven, ten days. It can't be done. Thus you get the reasons for these quick advances of the Germans; absolutely a question of men.

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In the Somme we advanced, but advanced slowly for the reason that we did not have sufficient men to shove them in and take the losses. The consequence was when the Hun position was prepared, the men would advance and take it, then sit tight there for weeks until another position was prepared and advance again all because we did not have sufficient men to rush through and take the other after once breaking the first line. That is the only way you take positions quickly over there.

We have never been able to do that. The German at times has been able to do that so the first thing every one has to keep in mind in this game is men and we can't get too many of them.

But in connection with that, especially as I am speaking before the Leather Chemist's Association, I am perfectly frank to say that in my best judgment I sincerely believe that it is a mistake to send the trained leather chemist to the front. I have advocated that in Canada right along; for a time they had a law whereby a chemist could not enlist without a special order of the Army Council. The idea of that is perfectly rational. After this war we have got a great big fight on and it is going to be a case where all the big industrial plants will need the results of the chemist's study.

That is unquestionably one of the greatest sources of strength of the German commercial machine and it has to be our strength. We have any amount of men. Why sacrifice the few that are well trained when they can do a jolly sight better work here at more needed work?

You will say right away, "Well, why did you go if you have those views?" Perfectly obvious—we had a voluntary system. As long as you have a voluntary system you can't let private views like that interfere. It is a question whether you go—whether you are a man or not a man. But it should not be a voluntary system. It should not be allowed. That is the point I tried and am trying to make. You may think it extreme. I have thought it out ever since I have been in France, and I am absolutely convinced of it. Industrial chemists should be exempted by law.

In France we started in at Messines, then up into Ypres and down in the Somme and then Arras so you see we had some experience. Not that I was in the front line all the time, but we had

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the experience of covering practically the whole length of line and in that line the places where these big advances have now gone over.

Take Messines, for example, or take the line as it was when we went out there in 1915. Why, right from Ypres, right down in the Somme (for we didn't go into the Somme then but the line was later extended into that district) way down through the entire British line, with an odd exception only, we were in a valley and the Germans on the heights looked straight down at us. At Messines they could at points look into our trenches and at Vimy Ridge also we were under absolute observation. I don't say they could see every man, but the movement in the trenches could be seen from the German position.

There were two dangers: First, the question of observation; second, drainage. We lived in mud and muck and slush the entire time, whereas the enemy was on high ground and lived in perfectly dry shelters. But during 1916-17 we succeeded in getting the Hun out of the entire high ground, Passchendaele, right straight through Wytschaete and Messines (with the exception of Lens) then Vimy Ridge and all the Somme district. By this last attack that has brought the Hun over now, he has absolutely recovered that same ground simply through men. Also in Somme and around Messines he has taken all that ground again and more, because we have held Kemmel since 1914 and people that don't know the district cannot begin to appreciate the gravity of the situation as it is there today.

At Ypres, for example, with the positions he holds now, there can't be any transport moving in an area back of the lines except at night. No transport moving in daytime! That was the condition in the old days even when he was not as close as he now is. You can't move in daylight for about 6 miles back of the line and that is what we have again got into, all through lack of men.

Now there are innumerable things I could tell you about over there. I am not going to tell about atrocities and all that sort of thing. The whole sum and substance is that the result as shown at the Western front is simply a nation gone mad. They have lost all sense of perspective relative to decency—every sense. That sums up the question on the one side. I could tell all sorts of personal stories. My own sergeant, right in front of Messines,

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sent into the attack there, or rather just preparatory to an attack, was shelled very badly. I crawled over to him to give him some instructions. We were flat on the ground on account of the star shells, and a shell hit so close that I thought it was goodnight. I turned to him to give him some instructions and found him up on his elbows and grinning from ear to ear. He said, "Isn't this fine, Sir?" All he saw was the spectacular side of it.

There are lots of chaps out there that do see that side, although there are a great many that see the practical side, too, and it is a very hard game. It is a very difficult game, and I think that it is getting stiffer all the time and the men that are over there need every possible support in every way that can be given them.

As Mr. Vogel said in his paper they are trying to see that all equipment that is sent them is of such a nature that they get the maximum comfort that is possible to give them for that is the proper way. Because they do suffer, and they suffer very badly. One time we marched back from Messines and got into the billets that night. They had a hot meal ready for the men and two-thirds of the squadron wouldn't touch it. They simply flopped down, equipment and all on, completely exhausted. When you get strong, healthy men forced to that degree of exhaustion they are pretty tired and have had a pretty strenuous time of it.

Now there is one point that, being a manufacturer, I might refer to, and that is the enermous strength of Germany's position to-day. Yesterday you were making plans for co-operation along various lines—getting together to pull together, to buy in bulk and many other schemes. That is all splendid. I am very glad to hear that it is going on but there is not enough of it. With the present position of Germany if she retains anything like the position she has to-day, it is my belief, will dominate completely. By her industrial connections and by her agreements right now, she controls not only the whole of Central Europe but Russia. Are we going to get any of that trade? You all know that you will get none of it unless she is forced to give some. But in return what is she going to ask for? That she be given all the trade she wants here in our countries. I think we should realize that strength and realize that at every move made and every advance forward over any territory, the very first thing she has done was to complete a commercial agreement with that country.

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They are talking commerce, thinking commerce. They can't carry on foreign commerce now, but they are planning it all for afterwards and the sooner we realize that point and work our schemes out on that basis the better it will be. Of course one of the easiest ways to do it is for us to absolutely control our raw materiels because we as the Allies do practically control the bulk of the raw materials of the world. And if our governments do get together and control raw materials, then we are jolly sure we will get a good share of commerce afterward.

Now in conclusion, one of the duties we have to do over here, which we are anxious to do, is to try and dispel certain false theories that have been spread here—various statements about the part or lack of part Great Britain has played. I am not going into that in any detail. I merely will say she has put some 7,500,000 men into the game to say nothing of her navy, and you all know pretty much what her navy has done—saved the world! But we are all anxious on our side of the line, I know, to get as good and clear and as close an understanding in this country and of this country as can be arrived at.

Don't misunderstand me. I am not talking on a basis of free trade or reciprocity or anything of that kind. I am not talking those subjects at all. I don't mean that; but a better understanding, and I do most earnestly hope one and all on both sides of the line will keep in mind that we have a war on now and that our first object is to hold our Allies together and get them together, and keep away from any form of legislation or anything else, the direct effort of which is going to be antagonistic to certain groups of Allies. It is not worth it. We have got to pull together and I hope both sides in this game will work for one common object, that is to bring this war to a successful conclusion. This is not a war where if we don't win we get out fairly well—if we don't win and completely win, we absolutely lose. There is no intermediate with us. There is with Germany, but not with us. We either win or we lose, and to win it is going to take every resource we have, and if we hold together and build up a great strength together, there is no reason when this is over why we should not have the most perfect friendships, the most wonderful harmony throughout all the English-speaking world.

In response to questions concerning the effect on the men's

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feet due to wearing chrome leather or vegetable-tanned or chrome re-tanned leather, especially as to chafing and heating of the foot through using these kinds of leather, Major Marlatt added the following observations:

In the old days there was practically no marching (of course these days there are big movements of troops) except up from the trenches to the billets and back again, and the rest of the time you stuck in the trenches. For example, you are there three weeks. Part of this time will be spent in the first line and immediate supports and only in one week of the three do you get any marching at all and then only a little for exercise sake and chafing only comes through marching.

All through France and Flanders it never gets very hot in any part we were in. Down in the Somme it probably did in the summer. I was not there in summer but elsewhere you wear big woolen stockings all the time and I don't think that question of heat affects the men who are in Flanders.

I can answer most decidedly the question of what the men would rather have. No man who was offered a chrome-tanned boot or bark-tanned boot would hesitate, but would take bark-tanned every time and the heavier it was stuffed the better he would like it.

SOLE LEATHER FOR ARMY USE.*

By Allen Rogers.
Pratt Institute.

In presenting a paper on such an important subject as sole leather for army use, I feel that the task is an undertaking of herculian magnitude. I must confess at the start that reliable information on the subject is very meagre, and I regret to say that so far as the literature is concerned practically nothing is available relating to this very important matter. Whatever information is available is based almost entirely on individual opinion and not upon systematic investigation. What we need is leather that will wear well, at the same time furnish comfort to the foot, and be reasonably waterproof. Whether this leather is oak,

* Read at the Atlantic City meeting of the A. L. C. A., May 17, 1918.

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hemlock, union, or even chrome, is immaterial so long as it gives results.

Specifications for leather have been drawn up to protect the Government, and although they provide for certain definite items we are not sure that they are correct. No doubt we all agree that the analysis of a good grade of sole leather should fall within certain limits, but can we take an analysis and say that because this leather falls within the prescribed limits that it will be a good wearing piece of leather? Rather would it not be far better to draw up a set of specifications saying just what hides should be used and just what tannage should be employed. No doubt this method would give a uniform product, but we do not know what tannage to suggest. Is it not time, therefore, for us to get together and by proper co-operation and systematic observation determine what leather should be used on our soldiers at home and abroad? We as tanners and leather chemists regret that it was necessary, as it is said, for Pershing to purchase shoes from England because our own shoes did not stand up in time of need. There is no reason why we cannot make as good a shoe as any other country, and the only reason that we may have failed is because we have never determined by actual wear tests just what leather gives the best service in field use.

In recent years extensive tests have been made by the Bureau of Chemistry and by the Bureau of Standards on the wearing quality of leather. These tests have been made under various conditions and with a large number of different kinds of leather. Analytical data has been taken and in some cases actual wearing tests as well as machine tests have been made. The information thus accumulated is interesting and may be of benefit at a later time, but again it does not tell us what we desire to know.

In order to arrive at the information necessary to the proper specification for sole leather for army use, a series of tests were recently proposed which provided for the actual wearing of 1,200 pairs of shoes by soldiers at one of the training camps. These shoes were to be made up in a number of ways, and of each kind 100 pairs were to be worn. That these tests have never been completed is due to the refusal of certain tanners to give the information requested as to the nature of the tanning materials em-

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ployed. Such a short-sighted policy is to be deplored, especially at a time when we should all try to work for the common good.

With the data before us that a series of tests such as the above would furnish we might then draw up specifications, based on facts, which would warrant us in assuming that our leather would be as good as the best that could be made. Is it not possible for us as an Association to use our influence to bring about the desired co-operation on this most important matter?

In the specifications now being used by the quartermaster's department certain requirements are set forth and it is to bring out discussion on the subjects that I propose to give the opinions expressed by several tanners and leather chemists. In reply to my inquiry a certain leather chemist makes the following statement:

"As long as it is permissible to put glucose and soluble salts into leather, I can see no use in requiring the determination of the nitrogen in the estimation of hide substance, even in unadulterated leather made by the long vat tannage. I would hesitate to set a limitation on such a factor, that would be fair and, at the same time, be of value in judging the quality of the leather. As a matter of fact I hardly think any one will quarrel much over the quality and extent of the tannage of our modern sole leather. From an economical standpoint it is wise for the tanner to completely tan the hide, and it is doubtful if any chemical specifications would aid much in bringing this about. Rather than a question of quality of tannage, the poor leather is probably due to excessive weighting with soluble materials. There are some tanners to-day, who honestly believe that leather is improved by the use of glucose and Epsom salts, on the ground that a sole of heavier iron can be produced by their use, and that the necessarily heavier iron sole will wear better than the lighter one.

"There is no doubt in my mind, and I base it on observation, experiments, and experience that the logical material for obtaining the necessary weight and firmness is pure tannin. The English recognize this, and it is a fact that leather filled with tanning extracts, within reasonable limits, by either the vat or drum processes, continues in the formation of leather substance by a union of uncombined tannin with the hide, even after the leather is finished and is in the warehouse, or in the shoes."

The specifications proposed by this chemists are as follows:

	Oak and union Per cent.	Hemlock Per cent.
Water soluble material	26.00	26.00
Total sugars or glucose	3.00	3.50
Total $MgSO_4.7H_2O$	1.00	2.00
Total ash	1.00	1.50
Oil	1 to 5	1 to 5

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In response to my letter in inquiry the following was received from another well-known leather chemist.

"We have been manufacturing sole leather exclusively since 1907 and during that time have endeavored to develop the highest possible grade of leather for finding purposes. The leather that we have found to give the highest commercial satisfaction and command the highest price analyzes as follows:

	Per cent.
Moisture	11.00-13.00
Water solubles	22.00-26.00
Grease	4.00- 6.00
Sugar	3.00
Ash	1.75
Hide substance	30.00-32.00
Combined tannin	26.00-28.00

"This is a leather that will, when placed under a 12-inch head of water, stand for 36 hours without the water penetrating through. This leather is produced in the straight vat tannage, requiring approximately five months. The leather as it leaves the lay-a-way contains approximately 39.00 per cent. hide substance. It is then filled with extract so that the finished product analyzes as mentioned above. We have made leather that was not extracted, tanned approximately in the same way, and have made leather that was more heavily filled than the one mentioned, neither of which gave the same satisfaction. The leather which was not extracted was too soft and did not have the water resisting nor the wear resisting qualities; although it was long fibered and a very pretty piece of leather in appearance. The more heavily filled leather was very short fibered, and resisted water penetration comparatively well, but not nearly as good as the standard piece first mentioned. The leather last mentioned gave on analysis about the following:

	Per cent.
Moisture	12.00
Water solubles	28.00
Grease	5.25
Sugar	5.10
Ash	1.75
Hide substance	29.00
Combined tannin	23.00

"From these experiments I make the following deductions: In order to have the proper wearing quality a piece of leather must be filled to sufficient extent to show combined tannin to from 26.00 to 28.00 per cent. This can only be accomplished by a long time in pure liquors in the lay-a-ways, and then the proper filling after the stock is tanned. I believe that the leather should not contain over 3 per cent. of sugar, which amount will take care of that in the tanning material and allow a small additional quantity to help in finishing. The ash should not be held too

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low as the best water resisting leather is produced by filling with a high non-tannin extract difficultly soluble in the cold. This class of extract usually carries a high per cent. of ash."

From another leather chemist the following ideas of specifications are of interest:

Moisture—Not over 15 per cent.
Ash—Below 2 per cent.
Oils and grease—Not more than 6 per cent. nor less than 3 per cent.
Free sulphuric acid—Not over 1 per cent. (Procter & Searle).
Water solubles—Less than 23 per cent.
Sugar as determined by glucosides—5 per cent. or less.

This chemist cautions against the use of excessive sugar and Epsom salts, and thinks that the stock should be well filled with tannin materials.

The opinion of several tanners who have been approached on this question seems to be that it is absolutely necessary to add glucose and Epsom salts in order to obtain a merchantable article. In one case a statement was made that the leather filled with sugar and salts appeared to give wearing tests superior to non-filled leather.

One point which seems to have escaped attention in connection with sole leather for army use is that the shoes have to be worn in all kinds of weather and under all sorts of conditions. No matter how good the tannage, the leather will eventually wet through unless completely waterproofed. Attempts at waterproofing are being made by the shoe manufacturer by applying a wax in a solution of volatile solvent. This method is useless because the solvent evaporates leaving only a small fraction of the waterproofing material in the leather. Oiling or dubbing will give no permanent result as here the proofing is only on the surface. There is only one way at present known to make a leather waterproof and that is to fill it to the limit with grease. Just what this grease should be, however, is open to discussion.

The opinion of a man who has made this his business for many years, is that the best waterproofing for finished shoes consists of a mixture of amorphous mineral wax and a fluid petroleum distillate. These two materials should be mixed together in such proportion as to give a compound melting at about 100° F. A mixture of this kind being unsaponifiable would not be affected by alkaline mud. On account of its high melting point it would

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become fixed in the fiber and so would not work through to stain the soldiers' socks, neither would it be drawn to the surface to be removed by dust. Its simplicity of application coupled with its extreme cheapness should warrant careful consideration.

Water rots leather more than any other agent. Therefore, if we not only waterproof the leather but at the same time protect the stitching, we will find that the question of water absorption has been eliminated and as a result the leather will not fail to give satisfactory service. England and France have found this to be the case; why not profit by their experience?

Although the speaker has quite decided views on the matter of tanning sole leather, and in regard to the filling of same, it will not be included as part of this paper. In closing, however, he wishes to again make a plea for the co-operation of tanners in making it possible to complete the extensive wear test planned several months ago, and which are being held up, because certain tanners are unwilling to furnish the information requested. The days of trade secrets have passed, and if we hope to place the leather industry on the highest plane of efficiency we must all get together and work for the common good.

THF WORK OF THE BUREAU OF STANDARDS IN LEATHER.*

By P. L. Wormeley.

Leather like all other materials has certain properties upon which its utility depends, such, for example as flexibility, durability, toughness, porosity, and the like. The relative magnitudes of the appertenant properties of materials is the factor which fixes their respective uses.

The problems involved, therefore, are first to determine the magnitudes of the several properties of the material, and second to correlate these properties with the uses to which they appear as a group to be best adapted. In laboratory practice the problem may be attacked initially from any angle, but a comprehensive program will eventually ramify until every point of view has been considered and provided for. The point at which the Bureau of

*Read at the Atlantic City meeting of the A. L. C. A., May 17, 1918.

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Standards encounters the subject of leather is in the careful determination or measurement of its useful properties with a view to ascertain what might be called natural standards of quality. We make leather on the basis of materials which nature affords. We are not building up a new material, but rather ascertaining the uses of a natural material which may be treated to enhance its natural utility. From this point of view the problem of leather research involves no difference in principle from the problem of research on any other material. The specific combination of properties alone determines the difference in treatment of the problem.

The Bureau of Standards grasps the subject of leather, as of other materials, from the point of view of standardization. Measurements are required at every point, measured numerical data which form the quantitiative description of a material are determined by experiment, standards of quality are developed—sometimes called specifications—which define in measurable terms the respective magnitudes of the constituent useful properties; then the standards of performance are agreed upon to test out, under service conditions and under simulated service conditions, usually with accelerated tests, the servicability of the material in question. Finally, standards of practice are agreed upon, as in a sense, a measured technical control of the processes by which the leather material is obtained, treated, sampled, tested, and utilized. Thus, the standardization as applied to leather is seen to involve numerical data, quality, performance, and practice—all determined and defined as standard in terms of units and standards of measurement. We must measure quality as truly as we have measured length, we must develop units and standards of quality for all materials and uses exactly as we have developed units and standards of length. That they are more complex is to be expected and we must naturally analyze the problem into its simplest elements, determine these by test and measure, and then synthetically combine the results and finally provide integrated or service tests in which the constituent properties act as a unit in determining the net efficiency of the material for its purpose. The Bureau's present treatment of the leather problem naturally falls for the most part, under the heading, "Standards of Quality."

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The personnel of our laboratory force both for chemical and physical work, as well as our laboratory space and equipment, which have been somewhat limited up to the present time, will be very much increased in the near future when we move into our new industrial research laboratory now under construction.

The Bureau is just now, particularly interested in a study of the physical and chemical properties of leather required for military purposes, and in this work we are fortunate in being favored with the hearty co-operation of the National Association of Tanners. The problem is of special importance at the present time in view of the large quantities of leather required for army uses, of which several may be mentioned.

The ordnance department has availed itself of the Bureau's laboratories in which two chemists devote their entire time to the investigation and analysis of equipment leather. During the past seven months more than 800 samples of leather have been analyzed and tested for this department. Physical investigations are also being conducted with the view of improving existing specifications for this class of leather, with special reference to strap and harness leather.

In connection with this work a series of tests is being made to determine any fixed relation between tensile strength, buckle shearing resistance, and tearing resistance at different parts of the hide. Sides of strap and harness leather have been blocked off and cut into rectangles from each of which specimens have been prepared for the three determinations. Buckle tests and tearing tests are also being made on samples representing leather delivered under contract.

Work is being carried on for the office of the quartermaster general, particularly in connection with shoe leather and fiber composition materials intended as a substitute for sole leather. In line with this work the Bureau is studying the relative merits of different waterproofing treatments both for sole and upper leathers.

To study the effect of waterproofing materials upon the wearing quality of sole leather, soldiers at Camp Meade, Md., are wearing half soles or "taps" of the same leather, the tap on one shoe being treated with waterproofing material, the other being used untreated.

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Service tests are being made to determine the relative water resisting properties of vegetable-tanned as compared with chrome re-tanned upper leather. In this case the shoes which are made with the right and left uppers of different leathers, are used under conditions that keep the uppers wet the greater part of the time. They are inspected after each day's wear and dried out before being used again. The soles being of the same material, the difference in the amount of water absorbed by the uppers is determined approximately by weighing before and after the shoes are dried.

There are unquestionably honest differences of opinion among tanners, manufacturers and consumers, regarding the relative value and wearing quality of different sole leathers and no thoroughly satisfactory specification or method of test has been developed.

During the past year the Bureau has conducted a series of preliminary experiments with a machine designed for testing the relative wearing quality of sole leathers. The indications of this machine in testing different portions of sole leather bends are fairly in accord with the observed behavior of similar portions of a bend in service. More extensive experiments are now being made with two of these machines to determine their indications as compared with the results obtained in service tests of different leathers on army shoes. This series of tests is being conducted with sixty oak tanned sole leather bends representing four commercial brands. Two of the brands are of low-water soluble content and contain a relatively small percentage of salts and glucose as compared with the other two which are rather heavily loaded. Each pair of shoes will be made with one sole of high water soluble leather and the other sole of low water soluble leather leather, the two soles being cut from the same location on the bend.

In addition to the experiments with high and low-water soluble leathers, the Bureau is studying the effect of different degrees of tannage and different methods of finishing on the wearing quality of sole leather. The general plan is to cut a hide down the middle and give the two sides the same treatment except for the point in question, thus eliminating all but one or two variables. Of five hides now under observation, two are being used to

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determine the relative wearing qualities of a belting tannage as compared with a sole leather tannage, two to determine the effect of loading with glucose, and one to determine the effect of a relatively large amount of grease. The procedure in this case is the same as that referred to in connection with high and low-water soluble leathers. Complete chemical analyses are being made by the Bureau of Standards and by the American Leather Research Laboratory to determine the variation in chemical composition at different parts of the bend. The results of these analyses will be used in correlating the chemical composition of different leathers with the physical properties as determined by laboratory and service tests.

The use of fiber composition soles on army shoes, particularly for repair work, has been suggested, and the Bureau is now making laboratory experiments in conjunction with service tests at Camp Meade to determine the adaptability of this material as a substitute for sole leather. The method of procedure has been to have one shoe of a pair soled with leather and the other soled with fiber composition. One of our representatives makes weekly inspections of the fifty pairs which are being used as a preliminary experiment. The results of our laboratory tests indicate that the wearing quality of the better grades of fiber composition soles compares favorably with that of good oak-tanned sole leather and this is in accord with the results thus far obtained from the service tests just referred to. It has been found that some of the composition soles have a tendency to crack, and to break at the stitches.

The Bureau has for a number of years acted in an advisory capacity for the various Government departments in furnishing specifications for miscellaneous materials and in making reports covering the results of tests in connection with supplies furnished on contract or submitted with competitive bids. In this way we frequently have occasion to analyze, and test samples representing strap leather, harness leather, leather belting, etc., for the Panama Canal and the general supply committee.

The Bureau, in collaboration with the Bureau of Fisheries, is investigating the problem of tanning shark and other fish skins. A large number of skins have been distributed among the various tanners who are experimenting with methods of producing tanned

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skins of a quality that may be used as a substitute for certain grades of leather. The experiments have not been successful in all cases, but a number of tanned skins submitted for test have given encouraging results. The Bureau is investigating the physical properties of skins tanned in different ways and it is thought that further experiments will develop methods of tanning by which fish skins may be made into leather adapted for useful purposes. One of our chemists is devoting his entire time to problems in connection with this work.

In conclusion I desire to say that the Bureau is anxions to co-operate with all agencies which have to do with progress in the leather industry. Any technical progress that is made in the field of leather utilization raises the standard of the entire industry. The Bureau is one of many factors working for such progress, and hopes to correlate its activities with the other agencies at work. Therefore, while its present investigations cover but a small portion of the field, it will be noted that the aim has been to attack the most practical problem connected with leather from the standpoint of the Government use of leather. This problem is the durability or wearing quality of sole leather. Other important problems are under investigation and these will fall into their proper places in the general scheme of leather research which the Bureau has in mind.

THE TESTING OF COAL TAR DYES FOR LEATHER.*

By H. R. Davies, Chairman.

As chairman of the committee appointed to consider the testing of Coal Tar Dyes for Leather, I regret to report that it was impossible to obtain the assistance of any collaborators owing to the fact that the present year has been a particularly hard one on most of the laboratories due to the excessive demands brought about by the war situation and the draft. Under the circumstances it was impossible to do any satisfactory committee work, and after consultation with Mr. Oberfell it was decided that this, report should take the form of a general review of the situation rather the accustomed form of a detailed description of work done.

* Read at the Atlantic City meeting of the A. L. C. A., May 18, 1918.

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The analysis and testing of dyestuffs is a problem that offers, when considered in its entirety, many confusing difficulties. The large number of products, varying in species, properties and composition, cannot be reasonably divided into classes all of which have definite characteristics upon which an analytical scheme can be based. Though many classifications have been proposed and adopted the fact still remains that a satisfactory analysis and examination of a dyestuff depends to a large extent upon the skill and experience of the individual observer.

It seems to the writer that it is not directly in the province of the A. L. C. A. to deal at all with the larger question of the general analysis of dyestuffs. This belongs purely to the realm of color chemistry and the literature on this subject is voluminous and can be readily referred to in case of need.

Perhaps the work of A. G. Green and his associates is the most thorough and comprehensive of all, and the methods of analysis which have been published by him in the year 1916 in a book entitled "The Analysis of Dyestuffs," represent the last printed word on this subject. The methods of analysis there given are the revised and completed results of a series of investigations lasting over 20 years.

Another published work on the same subject in the English language is that of S. P. Mulliken of the Massachusetts Institute of Technology, Vol. 3, of his "The Identification of Pure Organic Compounds," being devoted entirely to the identification of commercial dyestuffs. It is the writer's opinion, however, that this work while interesting, and to a certain extent of value, is not a method which can be followed blindly, as it is based upon an arbitrary dyeing method and does not take into account the fact that dyestuffs as sold are not pure organic compounds.

Apart from the general question of the analysis and identification of dyestuffs, however, there are two phases of the dyestuff testing situation which might very reasonably be the subject of further work of the A. L. C. A. These are briefly:

1. The testing of dyes for strength, shade and value with particular reference to their use on leather.

2. The laboratory testing of dyes as to their suitability for various purposes.

The committee work of last year dealt wholly with the testing

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of the money values of artificial dyestuffs, and both the committee report and the ensuing discussion brought out that there was practical unanimity of opinion on certain points.

1. As far as buying and selling is concerned a testing method on textile fibers could well be adopted. Though this was the general opinion expressed at last year's meeting and though it conforms with the general practice at the present time, it must be distinctly understood that the method of testing for value on textile fibers is confined absolutely to comparative tests of chemically identical colors.

2. That all dye tests should be made on a strictly comparative basis.

3. That it is difficult or impossible to obtain results on leather at all comparable for accuracy with those obtained on textile fibers.

There was some difference of opinion regarding the adoption of a standard yarn or textile material for use in all the laboratories. It is the writer's opinion based on a large experience in the testing of dyestuffs for all purposes, that this is not essential, though the matter could easily be made the subject of further work if it is deemed advisable. If tests are conducted on a comparative basis any difference which exists will show up almost equally well irrespective of the particular material on which the test is made. Another point brought up in the discussion by Mr. Yocum might be considered a little more fully. Mr. Yocum raised the point that the valuation of a dyestuff might readily be affected by determining chemically or analytically either the adulterant or the pure dyestuff. It might be said that there have been various methods proposed for the volumetric determination of dyestuff value. These methods, however, all fail in one respect. The primary use to which a dyestuff is put is to obtain a certain definite color or shade, so that any method which does not provide for this renders it obligatory that a comparative dyeing must always be made so that this important point can be determined. A method for the determination of adulterants in basic colors has been proposed by Atwood in which the basic color is dissolved out with anilin and the insoluable adulterants estimated, but the writer is not aware that the method has found any but the most restricted use.

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Dr. E. Knecht and E. Hibbert have done a large amount of work on the estimation of many synthetic dyes by the use of titanous chloride as a reducing agent. The dyes act as their own indicator and it is a simple calculation to determine from the amount of titanous chloride used the relative strength of the dyestuffs, providing that, (and this is where the method falls down) there is no reducible matter present which has not tinctorial value. In other words, the method is only suitable for practically pure dyestuffs. The results of this work have all been published in the *Journal of the Society of Dyers and Colorists* in the past seven or eight years.

There are other titration methods which are applicable only to certain individual dyes and these need not be considered in this connection.

I think the remark of Dr. Klaber that it is a very much easier proposition to determine the tinctorial strength than to look for all the possible adulterants, explains why we are forced to adopt the comparative dye trial as the logical method for the determination of the value of the dyestuff.

We now come to the second phase, namely, the laboratory testing of dyes as to their suitability for various purposes.

There is not the same unanimity of opinion here, held by some that the suitability of a dye for a given purpose can only be determined by an actual large scale trial. Others claim that it is possible to do in a dye testing laboratory anything which can be effected on the large scale and that dyeing formulae and methods can be transferred from the laboratory to the works and identical results obtained. The writer believes that the truth lies between these two opinions. There is no doubt that from laboratory dyeing made in jars it is possible to determine which of two different colors is the best for a given purpose and to determine which colors work well in combination. It is possible, also, to determine the level dyeing and penetrating properties and to approximately match any shade. When the process is transferred to the works it is quite likely that proportions may vary somewhat because conditions vary, but the variation is slight if the laboratory trial is carried out with a common sense appreciation and approximation of the actual tannery conditions.

It is the writer's opinion that much useful work can be done

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in the laboratory in the way of determining the most suitable combinations to be used to produce desired effects. For this work textile tests are of no use whatever. The textile tests must be confined purely to the valuation of a known dye against a known standard. All work which demands a choice between two or more colors of different properties and characteristics must be decided by a comparative test on the leather it is desired to dye and under as near an approximation to the actual tannery process as the laboratory can afford.

Under these conditions it will be seen that it is almost impossible to draw up any official methods for the testing of dyes without devising a large and comprehensive scheme that would be both cumbersome and inefficient. Dyes even of the same class vary enormously in their individual characteristics and the choice of the most suitable dyes can only be definitely determined by an actual trial, under either laboratory or tannery conditions, of all the dyestuffs available for the work in hand.

As a last word it can only be reiterated that the strictly comparative dye trial is the fundamental basis on which the whole fabric of dye testing is built and that this applies equally to leather, textiles or to any other material.

The above is a general survey of the situation as it exists. In addition, I might mention that some work has been carried out in the writer's laboratory but as it is by no means complete it is not proposed to describe this in detail but only to indicate the conclusions which may so far be drawn from the results now at hand.

Hearing from Mr. Delaney, Chairman of the Committee for Natural Dyes, that he contemplated making a series of experiments using standard hide powder for the determination of the value of natural dyestuffs, the writer has made in his laboratory a series of experiments with all classes of dyes on this material. The method adopted was to take a given quantity of standard hide powder, place in a shaking apparatus, together with definite quantities of dyestuff solutions. Tests were made with both chromed and unchromed hide powder. The hide powder was dyed and the color solution well exhausted in the majority of cases with the acid, direct and acid mordant dyestuffs. The basic

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dyestuffs had little or no affinity and in order to estimate the strength of these colors it was necessary to first mordant the hide powder with tannic acid. The results were, however, in all cases disappointing. An examination of the dried hide powder did not show that this method could be relied upon to show differences of strength or shade which were easily seen when the same dyes were dyed according to the methods advanced by Mr. Creese in his last year's report.

The hide powder method in the writer's opinion has only one point to commend it, and that is, the fact that the dyeings are made on a standard material which is practically always available instead of on textiles which are not ordinarily found in a leather chemist's laboratory.

The Council also requested that the Committee on Synthetic Dyes, at Mr. Lehmann's suggestion, endeavor to determine the practicability of using sulphide colors for the dyeing of leather. Many experiments have been made in our laboratory to see if it were possible to devise a method for the application of sulphur colors to leather. As a class the sulphur colors are cheap and are fast to light and most other color destroying agencies. They are generally used on cotton because of the fact that when dyed in a normal way the large amount of sodium sulphide necessary to effect the solution of these products precludes their use on all fibers of an animal origin. The same naturally applies to leather.

The large German color works and others have patented various processes for the use of sulphide colors on cotton and wool mixed goods. All of these methods depend on the use of an acid salt to neutralize the alkalinity of the bath and so render it possible to dye at low temperatures without dissolving or harming the wool. Experiments have been tried on leather using sodium bisulphite and sodium bilactate. It is impossible to give accurate proportions as these have been considerably varied according to the color used and the amount of sodium sulphide.

There is no doubt that sulphur colors, dyed according to these methods, can be applied to leather. The results obtained are generally not good. There is difficulty in obtaining exhaustion of the bath and the shades produced are not full and brilliant.

A similar process which has been recently patented in England

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and is known as the Lodge-Evans process, after the discoverers, seems to give somewhat better results. This process is based on the observation that if sulphur colors are boiled with sodium sulphite, previous to dissolving in sodium sulphide, any caustic alkali in the dye liquors may be almost neutralized by addition of ammonium salts without precipitation occurring. From these neutral or faintly alkaline dye liquors cotton and wool goods may be dyed, the extent to which both fibers are dyed depending largely upon temperature. It was thought that this method could be applied to the dyeing of sulphur colors on leather and experiments are now being carried out which seem to show more satisfactory results than those obtained by the older method of neutralizing with an acid salt. It is, however, the writer's opinion that there is no real demand that sulphur colors be employed on leather. The process must necessarily be complicated and depend for its successful use upon the correct amount of the various ingredients, which will change with each color. If the shades produced with sulphur colors were brilliant or full there would be some excuse for their use, but so far the results obtained do not seem to justify the additional trouble. It may be stated, however, that as far as penetration goes most of the sulphur colors we have so far tried penetrate extremely well. The method does not seem to be adapted for bark leathers, the only good results we have obtained being made on chrome upper leather.

The suggestion of Mr. Lehmann that sulphur colors being dissolved in sodium sulphide might be applied to the hide before tanning, has not been followed in any part of our work, as this seems to introduce complications which are a little beyond the scope of a Dye Testing Committee.

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TESTING OF DYEWOOD EXTRACTS.*

By C. R. Delaney, Chairman.

In relation to the testing of dyewoods, the standard method of testing, used in the majority of the dyewood extract laboratories, is to use worsted yarn of a certain fineness and weight. The worsted yarn is always a standard, as far as I am aware, purchased in large quantities, from the firms that make a specific yarn. There is always a question in my mind as to whether worsted should be used when the dyewood extract is going to be used for other purposes; that is, when the dyewoods are used in the cotton industry, a test on wool yarn is practically worthless.

Again, when the dyewoods are used in wall paper industry, for which they are used in very great amount, it is entirely useless to make a test on wool, or even on cotton, because they will not be representative of the way that color will be precipitated on such material as chalk and other of the inert bases that are used for the wall paper pigments.

In relation to the dye testing on leather, it is something that I have not been familiar with. I have made some experiments on some pieces of leather that I have received that have been used for the testing of the color of the tannin solutions, and I have found that the absorption of the dyewood is different for all kinds of leather, and therefore we could not use in our laboratories, this testing material, for the standarizing of our extracts.

It struck me that it might be well under these circumstances to test the material on a standard source of raw product, if I might call it that, and so Mr. McBride of the Imperial Dyewood Company, which is affiliated with Mr. John Kiel, made a very elaborate series of experiments upon the making of paper in which the dyewood extract was incorporated. He was always able to get his paper stock in such shape that he could duplicate the material at any time.

Now we could always get a hide powder of a reasonable standard, and I thought it might be well to see whether we could make a felt or a paper of hide powder, and therefore what few experiments I have made have been done along those lines.

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First of all, we took 5 grams of hide powder, put in about 200 cc. of water. Then we added to it varying amounts of mordants, they could be 1, 1½, 2 or 2½ per cent. of the weight of the hide powder, which is the way we dye-test on worsted yarn. Then, after the original water had been put in along with the hide powder, and the whole business shaken up in the shaking machine, which is about long enough for the mordant to strike, we added varying quantities of the dyeing material, and I found that we can exhaust the bath very nicely indeed, providing that we have the mordants adjusted for the dyestuff, just as, of course, we handle the wool, and I thought it might be well if I could outline to somebody here, to take up that work in a better shape than I could, the desirability of making these tests.

We can get a felt, but it is very difficult to make it cohere, so I have used a little glue to make a sort of a mat.

Now I have some results here with different proportions of dyestuff with the same amount of water, and varying proportions of water and the same amount of dyestuff, and I used some logwood extract, some quercitron extract, and some fustic extract which we have made. If you are interested in looking at those tests which are only preliminary tests, as only a sort of a mark to show the way that somebody else can take it up, I will show them to you.

They don't look pretty like dye-test samples do, but they do show the difference in result and I believe they can be made so they will be uniform, which is a great thing.

We used 1 per cent. of sulphate of iron, 1½ to 2½, and 1 per cent. of logwood, and there is practically no change there for the 1 per cent of logwood. It makes no difference with this sample.

On this one, we used 1 per cent. of sulphate of iron, and varying quantities of the logwood.

There is a change there, but it is not very appreciable. It isn't anything like the accuracy in comparison, you might call it, that we have with worsted yarn. But inasmuch as worsted yarn is no good in testing dyestuffs for leather, somebody has to do the work with hide powder or some similar material.

The method of procedure is very simple. The way that Mr.

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McBride does it, which is the best way for me to explain, is very much better than the way I got this out at the last minute. He takes a given quantity of paper pulp, white, and he stirs that up until every possible piece of it is in a very fine state, using a stirring machine specially designed to stir paper; (by the way, a special paper-stirring machine is nothing but a couple of pieces of wire in a beaker mechanically moved around), then, after all that is done, he takes this solution, or whatever it is, this mess out, and he pours it onto a copper funnel about 7 or 8 inches in diameter, and the funnel has a double section of brass gauze on top, about 200 meshes to the inch, and underneath that a supporting plate of copper.

Then, after he gets that out, he mixes it up with a little rosin size. I have used glue because I happen to have glue, and I don't happen to have any rosin size, but I think glue is just about as good. I use one part of glue to seven of distilled water. And then he simply dries that, either between blotting papers, which I did, or in a drying (paper calendering) machine—just a couple of steel rolls that are heated by means of a gas flame.

I thing this is about all that can be described. It is the simplest possible process, but the thing about this confounded hide powder is to get it to stick together, and after you get it to stick together, to prevent it from sticking to everything else. These were finished after being dried as much as possible with blotting paper. They were then put into a drying oven in between two pieces of oiled paper. I found that was the only way to prevent them from sticking, and then I cut them away from the oiled paper afterwards.

I used a vacuum pump with this filter.

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REPORT OF 1917-18 COMMITTEE ON COMPARATIVE ANALYSIS OF TANNING MATERIALS.*

By Robert W. Griffith, Chairman.

The Chairman was instructed to work on four solid tanning materials—two solid extracts and two raw materials. Sixteen members volunteered to serve on the Committee, all of whom reported their results.

Owing to advancing the time of the Annual Meeting, the Committee have not had as much time as is usually allowed for this work and some members have not had an opportunity to check their work, so that from the point of view of concordance in the results submitted, there is much to be desired.

The samples of powdered chestnut extract, solid quebracho extract, ground divi-divi and ground mangrove bark were carefully standardized in the Reed laboratories before being sent to the members of the Committee.

The Chairman instructed the members of the Committee to follow the Official Method of Analysis and called their attention to the following details, which they were requested to note on their reports.

First. Age and moisture content of original hide powder used. Hide powder which has dried in storage apparently has not the same absorbent qualities possessed by fresh hide powder.

Second. Acidity of chrome alum used for chroming hide powder. Chrome alum has various amounts of free acid; note the amount of free acid in chrome alum used.

Third. Note the temperature when chroming hide powder and when detanning.

It was suggested that attention to the foregoing details might account for some of the discrepancies which occur between chemists from time to time. The reports showed wide variations in some of these particulars, but perhaps owing to the introduction of other influences, they did not provide a basis for definite conclusions to be drawn therefrom.

Mr. T. A. Faust reported two complete sets of analyses on all of the four materials, using fresh hide powder containing 13.17 per cent. moisture for one set, and hide powder about a year old and containing 11.17 per cent. moisture for the other set. Both

* Read at the Atlantic City meeting of the A. L. C. A., May 18, 1918.

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results agreed so closely that it is clear that hide powder stored for a reasonable length of time does not affect the quality, and also that variations in the moisture of hide powder, when not too extreme, have no decided influence on the properties of the hide powder.

The acidity of the chrome alum used was determined by titrating a known solution with a standard alkali, phenophthalein being used as an indicator in most cases and the results expressed in terms of H_2SO_4. This method gave a basis for comparison, but the results obtained are not uniform with the variations in the acidity of the original chrome alum, and the probability is that the subsequent washing of the hide powder after chroming removes any excess of acid, so that the influence is neglible.

The greatest difference in the temperature at which the hide powder was chromed in the results submitted, is 5° C. and the temperature difference is the same in the process of determining the non-tannins, but apparently the influence of this variation in temperatures is not sufficient to affect the comparative results.

Too wide variation in the temperature at which the hide powder is chromed will, however, influence the determination of the non-tannins and it is recommended that the temperature of chroming and detanning the solution be kept within certain defined limits. This applies also to the temperature at which the hide powder is washed after chroming.

The closest determination between the members of the Committee occurs in the case of powdered chestnut extract, where the greatest difference is 2.64 per cent. tannin and the moisture difference is principally responsible for this.

The material which presented the greatest difficulties in securing uniformity was the sample of divi-divi, where the greatest difference in the tannin estimation is 12.28 per cent.

Both the raw materials used by the Committee are troublesome in the process of extraction.

In the case of the two solid extracts, it is noted that the greatest difference in the estimation of the tannin is caused by the variation in the determination of the insolubles, whereas in the case of the raw materials the difference in the estimation of the tannin is influenced by the variation in the determination of the non-tannin.

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POWDERED CHESTNUT EXTRACT.

Laboratory	Analyst	Tannin	Non tannin	Insolubles	Water	Total solids	Soluble solids	Method of cooling	H_2O in hide powd.	Acidity cr.alum	Temp. of chroming	Temp of detanning
A. W. Hoppenstedt.....	R. L. Moore	62.03	30.00	2.51	5.46	94.54	92.03	Slow	13	31.16	21°	25°
Kistler Leather Co.....	F. F. Marshall	62.68	30.18	2.78	4.36	95.64	92.86	—	12.63	29.07	20°	20°
C. C. Smoot & Sons.....	L. E. Stacy	61 12	30.84	3.48	—	95.44	91.96	Slow	15.5	27.7	—	—
Graton & Knight Co.	V. J. Mlejnek	61.16	31.18	2.65	5.01	94.99	92.34	—	13.32	—	21°-23°	20°-22°
Wm. F. Mosser Co.	Franz Urban	62.22	30.55	2.74	4.49	95.51	92.77	Slow	13.49	—	23°	20°
Faust-Yocum & Co.	F. A. Faust	61.04	32.17	2 45	4.34	95.66	93.21	—	13.17	13.56	21°	21°
Pfister & Vogel Co.	A. C. Orthmann	61.17	32.29	4.74	1.80	98.20	93.46	Slow	12.45	—	22°	21°-22°
Ashland Leather Co.	R. E. Porter	60.50	31.40	3.80	4.30	95.70	91.90	Slow	—	30.7	22°-25°	—
Elk Tanning Co.....	J. Johnson	62.80	30.49	2.85	3.86	96.14	93.29	—	12.5	—	21°	22°
Elk Tanning Co.....	J. E. McNutt	62.12	30.42	2.95	4.51	95.49	92.54	—	12.5	—	21°	22°
Leather & Paper Lab.	R. W. Frey	61.51	30.93	2 51	5.05	94.95	92.44	Rapid	10.55	29.4	23° 31°	24°
Champion Fiber Co.....	J. C. Dickson	62.74	30.08	2.17	5.01	94.99	92.82	Slow	12.92	28.75	22°	23°
Smethport Ext. Co.....	T. Blackadder	63.11	30.14	3.11	3.64	96.36	93 25	Slow	—	—	—	—
Jno. H. Heald & Co.....	T. G. Greaves	60.47	31.22	2.60	5.71	94.29	91.69	Rapid	13.4	27.76	25°	22°
J. S. Young & Co.....	H. Shaffer	61.33	31.76	2.74	4.17	95.83	93.09	—	12.19	—	26-28°	—
H. E. Young & Co.....	B. A. Gish	60.53	31.21	3.26	5.00	95.00	91.74	—	12.19	—	26-28°	—
	Average	61.65	30.92	2.95	4.44	95.54	92 58					
	Highest.....	63.11	32.29	4.74	5.71	98.20	93.46					
	Lowest	60.47	30.00	2.17	1.80	94.29	91.69					
	Greatest difference	2.64	2.29	2.57	3.91	3.91	1.77					

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Laboratory	Analyst	Tannin	Non tannin	Insolubles	Water	Total solids	Soluble solids	Method of cooling	H_2O in hide Powd	Acidity cr.alum	Temp. of chroming	Temp. of detanning
A. W. Hoppenstedt	R. L. Moore	42.09	25.76	3.40	8.88	71.25	67.85	Slow	13	31.16	21°	25°
Kistler Leather Co.	F. F. Marshall	49.65	21.29	2.18	9.20	73.12	70.94	—	12.63	29.07	20°	20°
C. C. Smoot & Sons	A. E. Stacy	52.43	21.17	4.90	—	78.50	73.60	Slow	15.5	27.7	—	—
Graton & Knight Co	V. J. Mlejnek	54.37	22.88	3.59	9.50	80.84	77.25	—	13.32	—	21°-23°	20°-22°
Wm. F. Mosser Co.	Franz Urban	50.88	20.90	2.99	8.72	74.77	71.78	Rapid	13.49	—	23°	20°
Faust-Yocum Co.	F. A. Faust	49.82	20.56	4.62	--	75.00	70.38	—	13.17	13.56	21°	21°
Pfister & Vogel Co.	A. C. Orthmann	47.05	27.75	6.17	9.10	80.97	74.80	Rapid	12.45	—	22°	21°-22°
Ashland Leather Co.	R. E. Porter	49.70	21.50	5.60	9.30	76.80	71.20	Slow	—	30.7	22°-25°	—
Elk Tanning Co.	J. Johnson	53.03	23.18	3.48	8.04	79.69	76.21	—	12.5	—	21°	22°
Elk Tanning Co.	J. E. McNutt	52.27	23.56	3.94	8.04	79.82	75.83	—	12.5	—	21°	22°
Leather & Paper Lab.	R. W. Frey	45.18	23.67	4.78	9.18	73.63	68.85	Rapid	10.55	29.4	23°-31°	24°
Champion Fiber Co.	J. C. Dickson	50.37	19.42	3.12	9.01	72.91	69.79	Slow	12.92	28.75	22°	23°
Smethport Ext. Co.	T. Blackadder	42.28	31.70	—	8.54	--	73.98	Slow	—	—	—	—
Jno. H. Heald & Co.	T. G. Greaves	49.96	22.97	4.31	9.1	77.24	72.93	Rapid	13.4	27.76	25°	22°
J. S. Young & Co.	H. Shaffer	50 89	19.76	4.35	—	75.00	70.65	—	12.19	—	26°-28°	—
H. E. Young & Co.	B. A. Gish	44.72	19.64	5.00	—	69.36	64.36	—	12.19	—	26°-28°	—
	Average	49.04	22.85	4.16	8.88	75.92	71.90					
	Highest	54.37	31.70	6.17	9.50	80.97	77.25					
	Lowest	42.09	19.42	2.18	8.04	69.36	64.36					
	Greatest difference	12.28	12.28	3.99	1.46	11.61	12.89					

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MANGROVE BARK.

Laboratory	Analyst	Tannin	Non tannin	Insolubles	Water	Total solids	Soluble solids	Method of cooling	H_2O in hide powd.	Acidity cr.alum	Temp. of chroming	Temp. of detanning
A. W. Hoppenstedt	R. L. Moore	34.59	10.83	4.18	8.92	49.60	45.42	Slow	13	31.16	21°	25°
Kistler Leather Co	F. F. Marshall	35.72	11.23	4.17	9.91	51.12	46.95	—	12.63	29.07	20°	20°
C. C. Smoot & Sons	L. E. Stacy	37.03	11.17	4.30	—	52.50	48.20	Slow	15.5	27.7	—	—
Graton & Knight Co	V. J. Mlejnek	39.42	12.40	4.53	9.94	56.35	51.82	—	13.32	—	21°-23°	20°-22°
Wm. F. Mosser Co	Franz Urban	36.36	11.22	3 65	9.58	51.23	47.58	Rapid	13.49	—	23°	20°
Faust-Yocum Co	F. A. Faust	35.52	11.13	3.27	—	49.93	46 65	—	13.17	13.56	21°	21°
Pfister & Vogel Co	A. C. Orthmann	36.61	12.27	3.46	9.81	52.34	48.88	Rapid	12 45	—	22°	21°-22°
Ashland Leather Co	R. E. Porter	36.35	11.20	3.65	10.00	51.20	47.55	Slow	—	30.7	22°-25°	—
Elk Tanning Co	J. Johnson	38.07	11.52	2.36	9.10	52.95	49.59	—	12.5	—	21°	22°
Elk Tanning Co	J. E. McNutt	38.37	11.34	4.81	9.10	54.52	49.71	—	12.5	—	21°	22°
Leather & Paper Lab	R. W. Frey	36.10	11.18	3.16	9.87	50.21	47.28	Rapid	10.55	29.4	23°-31°	24°
Champion Fiber Co	J. C. Dickson	38.68	11.65	4.95	9.71	55.28	50.33	Slow	12.92	28.75	22°	23°
Smethport Ext. Co.	T. Blackadder	39.68	13.22	—	9.66	—	52.90	Slow	—	—	—	—
Jno. H. Heald & Co	T. G. Greaves	36.90	10.75	3.96	—	51.61	47.65	Rapid	13.4	27.76	25°	22°
J. S. Young & Co	H. Shaffer	36.55	12.24	3.60	—	52.39	48.79	—	12.19	—	26°-28°	—
H. E. Young & Co	B. A. Gish	36.52	11.27	4.52	—	52.31	47.79	—	12.19	—	26°-28°	—
	Average	37.03	11.53	3.66	9.60	52.23	48.56					
	Highest	39.68	13.22	4.95	10.00	56.35	52.90					
	Lowest	34.59	10.75	2.36	8.92	49.60	45.42					
	Greatest difference	5.09	2.47	2.59	1.08	6.75	7.48					

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SOLID QUEBRACHO EXTRACT.

Laboratory	Analyst	Tannin	Non tannin	Insolubles	Water	Total solids	Soluble solids	Method of cooling	H_2O in hide powd.	Acidity cr.alum	Temp. of chroming	Temp. of detanning
A. W. Hoppenstedt	R. L. Moore	71.93	7.36	9.42	11.29	88.71	79.29	Slow	13	31.16	21°	25°
Kistler Leather Co.	F. F. Marshall	72.71	7.60	10.45	9.24	90.76	80.31	—	12.6	29.07	20°	20°
C. C. Smoot & Sons.....	L. E. Stacy	70.64	9.48	9.14	—	89.26	80.12	Slow	15.5	27.7	—	—
Graton & Knight Co.	V. J. Mlejnek	73.51	7.59	8.09	10.81	89.19	81.10	—	13.32	21.3	21°-23°	20°-21°
Wm. F. Mosser Co.	Franz Urban	73.34	7.42	9.77	9.47	90.53	80.76	Slow	13.49	—	23°	20°
Faust-Yocum Co.	F. A. Faust	72.35	9.12	8.55	9.94	90.06	81.51	—	13.17	13.56	21°	21°
Pfister & Vogel Co.	A. C. Orthmann	67.50	8.96	15.79	7.75	92.25	76.46	Slow	12.45	—	22°	21°-22°
Ashland Leather Co.	R. E. Porter	69.45	8.80	11.55	10.20	89.80	78.75	Slow	—	30.7	22°-25°	—
Elk Tanning Co.....	J. Johnson	73.13	7.88	10.15	8.83	91.17	81.01	—	12.5	—	21°	22°
Elk Tanning Co.....	J. E. McNutt	72.55	7.61	9.10	10.73	89.27	80.16	—	12.5	—	21°	22°
Leather & Paper Lab.	R. W. Frey	74.09	7.43	7.39	11.09	88.91	81.52	Rapid	10.55	29.4	23°-31°	24°
Champion Fiber Co.....	J. C. Dickson	72.07	7.43	9.52	10.98	89.02	79.50	Slow	12.92	28.75	22°	23°
Smethport Ext. Co.....	T. Blackadder	72.87	7.17	9 51	10 45	88.95	80.04	Slow	—	—	—	—
Jno. H. Heald & Co.	T. G. Greaves	70.17	8.17	10.66	11.00	89.00	78.34	Rapid	13.4	27.76	25°	22°
J. S. Young & Co.	H. Shaffer	73.93	8.11	9.21	8.75	91.25	82.04	—	12.19	—	26-28°	—
H. E. Young & Co.	B. A. Gish	71.26	8.29	10.12	10.33	89.67	79.55	—	12.19	—	26-28°	—
	Average	71.96	8.02	9.90	10.05	89.86	80.03					
	Highest.....	74.09	9.48	15.79	11.29	92.25	82.04					
	Lowest	67.50	7.17	7.39	8.75	88.71	76.46					
	Greatest difference	6.59	2.31	8.40	2.54	3.54	5.58					

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It is recommended that the method of procedure for the extraction of raw materials be elaborated.

It is requested that all members of the Association will use the form of report officially adopted by the Association.

COMMITTEE REPORT.*

Mr. Small's Modification of the Hydrochloric Acid-Formaldehyde Method for Separating Tannins, with Special Application to Chestnut Oak Bark and Chestnut Wood.

By T. G. Greaves, Chairman.

The fact that Mr. Small's method for the quantitative determination of pyrogallol tannins, especially chestnut wood extract, in admixture with chestnut oak bark extract, using the formaldehyde-hydrochloric acid reaction, had come into general use without having been used in committee work led to the appointment of this Committee to find what concordance could be expected between different laboratories, and to draw results from a wider range of samples.

As the Committee was appointed to work with the method as published in the JOURNAL, March, 1911, the only changes in the procedure which were made resulted from conferring with Mr. Small. As he did not feel that it was safe to allow the filtered solutions to set over night because of possible decomposition, and as fourteen or fifteen hours are required to complete the work, it seemed to be necessary to make a change to bring the method into the limits of a working day. Few laboratories have a competent night watchman to change the dishes from the steam bath to the oven after they have come to dryness, as is the case in the Graton & Knight laboratory, so the dishes are allowed to stay on the steam bath overnight, and are then dried in the combined evaporator and dryer for four hours more.

The Chairman noticed that a part of the residue pops out of the dishes at some time during the drying, both when the solution is brought to dryness on the steam bath, in the regular way, and when the evaporation takes place in the oven. The popping seemed to be confined to the residue from the filtered solutions, *i. e.*,

* Read at the Atlantic City meeting of the A. L. C. A., May 18, 1918.

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those which did not contain the precipitate. It was quite variable and sometimes seemed not to occur at all. Although this is a serious objection to the use of the method, it is probably one that can be overcome by further observation and discussion. This seems the more likely because six of the ten committee men did not have this trouble.

Notes from the letters of the committee men follow:

MESSRS. SELTZER AND MARSHALL: We noticed no popping.

DR. BLACKADDER: We have not been troubled with the popping which you mention. Perhaps you do not have sufficient escape for the steam from the steam bath, with possibly a higher temperature.

MR. DOWNING: I did not notice any popping, even with the white paper under the dishes.

In general, Mr. Small's work seems to be confirmed.

MESSRS. YOCUM AND KERNAHAN: We watched for this (popping) in particular, and in no case did we find that it occurred, so that what lack of duplication we found could not be due to this cause.

MR. DICKSON: I discovered no popping of the residue.

MR. PORTER: I have not noticed popping, either on the steam bath or in the oven.

It is well known that materials from different localities require different constants. I have found differences between Virginia and North Carolina materials.

I have obtained practically as good results using bromine water instead of the Stiasny reagent, with a little change in the precipitate weight constants.

Perhaps by using corrections it will not be necessary to filter the analytical solution used.

I hope that we can get some good results and adopt at least a provisional method.

MR. MLEJNEK: Some residue is lost by popping, as is shown by the white paper placed under the dishes. Whether or not the free circulation of air about the dishes during the long period of drying causes a spasmodic cooling with consequent popping, and how much is lost in this way, I am not prepared to say. The old method gives closer duplicates than those obtained by using the changed method.

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I believe further investigation along the line of this important question should be made, and a convenient and reliable method which is capable of interpretation developed.

MR. GISH: There does seem to be a tendency in this direction (popping), but I was not able to note any great variation from this cause.

MR. RIETHOF: I believe it (popping) happens sometimes, but it does not seem to affect the results materially. It might be possible to add some medium to the solution which would hold the residue together without influencing the results.

Among my reports you will find one of hemlock extract. The filtrate from the formaldehyde precipitation was practically colorless, and the duplicates checked surprisingly well. You know some extract manufacturers grind some chestnut wood into their hemlock leaches,—as they say, for better leaching, and sell the product as pure hemlock extract. It might, therefore, be of great benefit to establish the factor for hemlock. One ought to be careful about using factors given by strictly tannery chemists because they might get extracts that are not pure.

Mr. Riethof submits on pure hemlock extract the precipitate weight, 0.1984. The Chairman had obtained the precipitate weight 0.2261 and made the same observations as to filtrate and agreement of duplicates. Each tested only one sample, but these were of widely different origin. As soon as other figures are obtained, a factor can be taken and this method can be used for hemlock without any change in the procedure.

It is to be remembered that Mr. Small, in his original article, said that the method could be easily extended to other materials.

EXPLANATION OF THE TABLE.

The figures in the table, which are given to four decimal places, are the average precipitate weights obtained by each operator. As these mean little to anyone who has not used the method, the results are figured to the per cent. of extract which they represent. To do this, some figures must be more or less arbitrarily taken to represent the typical precipitate weights of chestnut oak bark and chestnut extracts respectively. The figures which have been used in most laboratories, 0.1600 for chestnut oak bark

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No.	Chemist	Sample No. 1 chestnut oak bark extract		Sample No. 2 chestnut extract		Sample No. 3 chestnut extract		Sample No. 4 chestnut oak bark extract		Samp. W-1 chestnut wood	Sample B-1 chestnut oak bark
		Ppt. wt.	Per cent.	Ppt. wt.	Per cent.	Ppt. wt.	Per cent.	Ppt. wt.	Per cent.	Ppt. wt.	Ppt. wt.
1	Blackadder, Dr. Thos	0.1579	1	0.0240	94	0.0321	88	0.1748	—10	0.0074	0.1945
2	Dickson, J. C.	0.1592	1	0.0206	96	0.0173	98	0.1782	—13	0.0147	0.1697
3	Downing, J. S.	0.1537	4	0.0338	87	0.0306	89	0.1912	—22	0.0063	0.1615
4	Gish, B. A.	0.1380	15	—	—	0.0174	98	—	—	0.0104	—
5	Greaves, T. G.	0.1580	1	0.0241	94	0.0183	98	0.1855	—18	0.0132	0.1955
6	Mlejnek, V. J.	0.1569	2	0.0320	88	0.0242	94	0.1824	—15	0.0198	0.1928
7	Porter, R. E.	0.1558	3	0.0250	90	0.0240	94	0.1730	— 9	0.0145	0.1875
8	Riethof, Oskar	0.1615	—1	0.0256	93	0.0206	96	0.1795	—13	0.0171	0.1886
9	Seltzer, J. M. and Marshall, F. F.	0.1594	0	0.0313	89	0.0220	95	0.1738	—10	0.0050	0.1480
10	Yocum, J. H. and Kernahan, C. M.	0.1525	5	0.0255	93	0.0215	96	0.1794	—13	0.0151	0.1858
	AVERAGE	0.1572	2	0.0273	92	0.0228	95	0.1798	—14	0.0132	0.1845
	Omitted from aver.	No. 4	No. 4	None	None	None	None	None	None	No. 9	No. 9
	Highest	0.1615	—1	0.0338	96	0.0321	88	0.1912	—22	0.0198	0.1955
	Lowest	0.1380	15	0.0206	87	0.0173	98	0.1730	— 9	0.0050	0.1480

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extract and 0.0150 for chestnut extract, have been generally considered to give credit for all the chestnut oak bark extract present. A few samples of chestnut oak bark run below 0.1600 but not many. The formula which is generally used for mixtures:

$$x = \frac{0.1600 - \text{the precipitate weight}}{14.5} *$$

where "x" is the per cent. of chestnut wood extract present, is based on these figures. It was used to obtain the per cent. results found in the table.

From the table, the average precipitate weight obtained for Sample No. 1 is seen to be 0.1572 and for Sample No. 4, 0.1798, corresponding to 2 per cent. chestnut extract and 98 per cent chestnut oak bark extract for No. 1, and —14 per cent. chestnut extract and 114 per cent. chestnut oak bark extract for No. 4. As both samples are pure and representative chestnut oak bark extracts, the results show that the method, being based on the figure obtained for the precipitate weight, which is not the same for all samples, cannot be classified as an exact method of analysis, but, as Mr. Small has said, it is the best method available for the determination. It shows if a chestnut oak bark extract contains any considerable amount of chestnut extract, and is useful in detecting accidental mixing, due to leaking valves, or willful adulteration. Roughly, approximate results can be obtained on "half and half" where set precipitate weights are used for the calculation; better results could be obtained if the precipitate weights of the two extracts entering into the mixture were known for each individual lot of "half and half."

The chestnut extract Samples, No. 2 and No. 3, are also pure extracts, although the formula generally used, based on 0.0150 preceipitate weight, would indicate that they contain 8 per cent and 5 per cent of chestnut oak bark extract, respectively. The precipitate weights of the raw materials sent out were not figured to per cent. The average results were: Chestnut oak bark, 0.1845 and chestnut wood, 0.0132.

It is of interest to note that the bark of the chestnut tree, which is usually left on, has considerable influence on the figure obtained by this method because its precipitate weight is greater than

* Derived from $\frac{0.0150x + 0.1600\ (100 - x)}{100}$ = precipitate weight.

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that of the wood. We obtained the precipitate weights, 0.0841 and 0.0795, average 0.0818, on a sample which analyzed 7.96 per cent. of tannin. Only one sample was tested. Allowing for the bark to be 10 per cent. of the weight of the wood, the effect is as follows: If the sample of wood alone were 0.0150, the figure for the wood with the bark on would be 0.0217, or if the figure for both together were 0.0150, the wood without bark would give the figure 0.0076.

Not enough samples were sent out to re-establish what figures it would be advisable to use as a basis for the formula which is in use, but these samples tend to confirm the figures previously given.

The agreement between different laboratories can be best judged from the per cent. column in the table.

The Committee has not attempted to cover the varieties of oak bark.

Other figures submitted by the committee men follows:

MR. MLEJNEK: Ground oak bark, 0.1899, 0.1867, 0.1879, and 0.1875.

MR. RIETHOF: Chestnut extract made by Cherry River Extract Co., 0.0156, 0.0166, 0.0213, 0.0201. Dry chestnut extract sent out by Committee on Comparative Analyses, 0.0180. Composite sample chestnut oak bark, 0.1940.

DR. BLACKADDER: A sample of chestnut extract made by Smethport Extract Company, 0.0274.

It seems possible that the figure for chestnut oak bark may vary from some cause or causes, perhaps the season or the age of the bark, or the locality, besides the variation which would be ordinarily expected.

Duplicate tests sometimes agreed closely and sometimes did not with almost every operator. In general, it seems that duplicate tests should always be run, except in the case of chestnut oak bark extracts, which are running easily on the safe side of 0.1600. To give an idea of what can be expected from duplicates, a table of the greatest variations between the highest and the lowest precipitate weight obtained by each operator on Sample No. 1 to Sample No. 4 inclusive, is given, together with the number of tests made on each sample. Names are omitted and the order is changed. Three committeemen are not included because they did not report duplicates corrected to a tannin basis.

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NUMBER OF TESTS MADE AND GREATEST VARIATION.

Operator	Sample No. 1		Sample No. 2		Sample No. 3		Sample No. 4	
	Number of tests	Greatest variation	Number of tests	Greatest variation	Number of tests	Greatest variation	Number of tests	Greatest variation
a	3	0.0157	3	0.0154	9	0.0195	7	0.0124
b	2	0.0125	2	0.0026	2	0.0054	2	0.0063
c	2	0.0010	4	0.0105	3	0.0035	4	0.0125
d	12	0.0250	4	0.0057	2	0.0002	6	0.0043
e	2	0.0013	2	0.0004	2	0.0008	2	0.0054
f	2	0.0024	2	0.0046	2	0.0032	2	0.0030
g	2	0.0034	2	0.0003	2	0.0035	2	0.0023

COMMITTEE INSTRUCTIONS.

The following instructions were sent to the committeemen:

Prepare a ½ per cent. solution of HCl and adjust by titration, making up enough for all of the work (or making and testing a 5 per cent. solution and diluting 1:10 for use). Make up a 2 per cent. formaldehyde solution. Mix these 1:1 immediately before using.

Make up the solution of the sample to be tested by the slow cooling method, to contain as nearly as practicable 0.4 gram tannin per 100 cc. Start the soluble solids filtration by the official method as soon as possible the next morning, using two funnels for each test (four funnels for each sample where duplicate tests are to be made). Two funnels are used in order to get 160 cc. of filtrate as soon as possible. The first 160 cc. of the combined filtrates, from the two funnels, is then used for the formaldehyde-hydrochloric acid test, and the next 160 cc. of the combined filtrates, from the two funnels, is pipetted for soluble solids.

To 50 cc. of the clear soluble solids filtrate in a crystallizing dish, add 50 cc. of the formaldehyde-hydrochloric acid mixture, and to 100 cc. of clear soluble solids filtrate in a 250 cc. volumetric flask, add 100 cc. formaldehyde-hydrochloric acid mixture. Cover the dish with a watch glass and place both it and the flask on adjacent openings of a steam bath. Heat with a good flow of steam for two and a half hours; remove; allow the flask to cool one-half hour in the air, then cool to 20° C. with water at 19° C. Make up to the mark, mix thoroughly and filter as for soluble solids by the official method, discarding the 75 cc. used for di-

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gestion and collecting for use only when the filtrate is clear. Keep funnels covered with a watch glass throughout.

Pipette 125 cc. of the clear filtrate into a crystallizing dish and place both it and the solution in the other crystallizing dish, after adding 25 cc. of water to the latter, on a steam bath and leave them there fifteen hours (overnight). The next morning, dry the bottoms of the dishes with a towel, place them in the combined evaporator and dryer and leave them there for four hours. Remove, cool in desiccators and weigh. Subtract the weights of the residues and correct for any variation from 0.4 gram tannin to 100 cc. of solution.

If a steam bath that can be run overnight is not available, the dishes may be left covered overnight and evaporated to dryness on a steam bath next morning, then removed and kept covered until evening, when they are placed in the evaporator and dryer and left fifteen hours (overnight).

The Chairman wishes to thank those who have served on this Committee for the work which they have contributed, and to suggest that individual work, or another committee, take up some of the points not covered in this report; for example. The Influence of Locality or Season on the Precipitate Weight, the Determination of Constants for Other Material and Varieties of Oak Bark, or The Revision of the Method.

NOTES ON THE PROCTER-HIRST TEST FOR SULPHITE-CELLULOSE.

By J. H. Yocum and E. S. Nelson.

Following up the work on the Procter-Hirst test, part of which we reported in a letter to this JOURNAL,* 80 grams of ground spruce wood was treated with 300 cc. of a 25 per cent. solution of caustic soda for 6 hours at 100° C. About 150 cc. of water was then added. It was filtered through a rag, and was then nearly neutralized with hydrochloric acid, being kept on the alkaline side, then filtered through paper.

1. The wood liquor alone was then tested by the Proctor-Hirst method, and there was no precipitate until after 24 hours standing, when a slight precipitate appeared.

* May, 1918.

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2. Fifty cubic centimeters of the liquor was added to 4 cc. of acid sodium sulphite (without heat), and immediately there was a slight precipitate.

3. Fifty cubic centimeters of the liquor was heated with 4 cc. of acid sodium sulphite, and there was a heavy precipitate at once.

4. The acid sodium sulphite liquor alone showed a slight precipitate on standing.

After several days, the liquor was filtered again, and the above tests repeated, with the following results:

1. Wood liquor alone—No precipitate.

2. Slight precipitate.

3. Heavy precipitate.

4. Slight precipitate on standing.

Not the slightest sign of a precipitate was noticed in the wood liquor alone.

After this, we tried the following:

Fifty cubic centimeters of the liquor was evaporated with 4 cc. of acid sodium sulphite until the sodium chloride and other salts were largely precipitated. It was then filtered, and the filtrate set to one side. This filtrate gave a slight precipitate by the Procter-Hirst test. The precipitate was then washed with a saturated solution of sodium chloride.

The precipitated salts, when dissolved in water, gave no precipitate by the Procter-Hirst method. However, on combining the solutions of the precipitated salts and the filtrate, a heavy precipitate was formed by the Procter-Hirst method. This precipitate may have been aided by the presence of salt (NaCl) in the precipitate used.

All these reactions seem to confirm the statement made in our letter to the JOURNAL, that the lignones of themselves, do not react with the Procter-Hirst test, but that the presence of the sulpho-radicle in an organic complex, apparently does precipitate.

It would appear to us, therefore, that the method of determining the presence of sulphite-cellulose liquors in tanning solutions, needs further study, and that too much credence cannot be given to this test.

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PROBLEMS FOR THE CONSIDERATION OF THE AMERICAN RESEARCH LABORATORY.*

DISCUSSION.

V. A. WALLIN: It seems to me in the first place, that Mr. Small's paper is full of splendid suggestions for the research laboratory. It brings to my mind the thought that it will be necessary to have steadily the continued co-operation of such men as Mr. Small and the men connected with the Chemists Association if we are to continue this American Leather Research Laboratory. That agglomerate with an algebraic echo will never appeal to the tanner sufficiently so that he will stay by this proposition until results are obtained.

The matter involves a science and a training that is way beyond the average tanner to appreciate or understand to the extent, that will give him necessary patience. That equation referred to by Mr. Small of course would be looked upon by most tanners as something they had no patience with at all, but you chemists seeing below the surface where the tanner can't see at all, can have an appreciation of the possibilities that are going to come out of this purely scientific problem, and say to the tanner, "Now, hold on, boys, something is likely to come out of that." This is the only way the fundamental can be brought to the surface and made valuable. And so I trust that the American Leather Chemists Association will keep in close touch with the American Leather Research Laboratory, otherwise I fear that unless the tanners see some development in the course of a year or two whereby they can make great economies or increase production or in some way turn this formation into the one thing needful for any business success—that is money, they will begin to get discouraged with their laboratory; and so it is up to you more scientific men to keep the men with whom you are associated in the tanneries in touch with the laboratory, its work, and the possibilities of its work.

I like that phrase, "interpretive chemist." The chemist must interpret the work of this laboratory to the tanner, and stay his patience and keep him satisfied.

I won't refer to any of the suggestions for actual work by the

* Original paper read at the Atlantic City meeting and published in this JOURNAL, June, 1918, pp. 239-248.

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laboratory, except one thought that comes in my own mind, and that is, that this laboratory could well do a practical work in co-ordinating the work of other organizations. The industry is getting to be very large, and covers a very wide field of usefulness, and is now covering a wide field of research. One of the very serious problems in Washington that has been evident in all of the war activities, has been the duplication of effort and the necessity of co-ordination of effort.

It seems to me that a part of Mr. Churchill's work could well be to keep his fingers on the pulse of experimental work and get all of these various organizations which have an opportunity for service working as a team—the Bureau of Standards, the Mellon Institute, the Leather and Paper Laboratory, the individual laboratories, and particularly the possibilities for unified work in the American Leather Chemists Association.

Now if Mr. Churchill is not only a research chemist, but if he is also a captain in industrial chemistry that can organize this work so that it does not duplicate, so that it all works harmoniously together—perhaps not for one end, but for several ends which do not conflict with each other, there, I think, the research laboratory has a splendid field for service.

DR. ALLEN ROGERS: Mr. Chairman, I would like to suggest that one of the problems for the research chemist is to study the degree of tanning in different stages of the process. Most tanners in making an inventory of the yard, assume that the stock is half tanned; then take the amount of material that goes in, the amount of material that is supposed to be in the hide, and the amount that is in the pits, and when they come to make their estimations find that they often fall short several thousand dollars.

During the past year as well as on several previous occasions I have worked along this line, and in every instance find that the yard is more than half tanned, that, in fact, when the hides come out of the second layer they are about four-fifths tanned. The leather is four-fifths tanned in about forty days, and the other sixty days is required for completion of the tannage, so it is not quite right to assume that the yard is half tanned. I bring this up because it makes quite a difference in dollars and cents.

MR. WILSON: Mr. President, there are a great many problems confronting the tanners which I believe cannot be solved

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without first getting at fundamental principles. Objection has been raised to working from this standpoint because most tanners lack the specialized training necessary to an appreciation of methods of solving their problems which require the employment of higher mathmatics or the intricate laws of physical chemistry. Although I doubt that the majority of tanners would be patient enough to wait for several years to see the results of methods they do not understand, still I feel firmly convinced that only by striving to get at fundamental principles can we hope to make progress of the right kind.

My firm has been much interested in this matter for some time and it has seemed to us that this research should be conducted at a great university where the men engaged could have the aid and counsel of leaders in all branches of the science who themselves are continually engaged in research of the highest order. With the object of putting this view to an actual test, my firm engaged Dr. Thomas of Columbia University to undertake research in leather manufacture, the first problem being an investigation of the mechanism of chrome tanning. Unfortunately for this undertaking, the Government required Dr. Thomas' services as a food expert and he is now "somewhere in France," a Captain in the Sanitary Corps of the National Army. Although this necessitates a break, the work will go on; in fact two papers have already been completed for publication. Until certain underlying facts have been discovered, these papers will probably be of such nature that the tanner will require his chemist to interpret them, but I have no doubt that ultimately the practical value of this work to the industry will be proved. The results are to be published freely for the benefit of all who care to use them and I feel sure that you will all be interested in following the progress of the work.

MR. H. H. HURT: One phase of the Research Laboratory that must not be overlooked is that it is largely up to the American Leather Chemists Association to see that a success is made of it. The National Association of Tanners have started a research laboratory, backed by the tanners' money, to examine the problems of the tanners, and we chemists should each take a personal interest in this proposition and do every thing possible to hold up Mr. Churchill and see that it is a success.

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PREPARATION OF HEAVY LEATHER SAMPLES FOR ANALYSIS.*

Discussion.

In the discussion which followed the reading of this paper the following points were brought out:

The dust caused by the draught from the fast revolving saws might be prevented to a great extent by lowering the axis of the saws two or three inches below the surface of the table. Having a funnel-shaped receiving arrangement for the ground leather, the small end of which terminated at least 12 inches below the saws also may help.

Better results as to moisture and soluble solids were obtained when the saws were run fast and the leather fed as quickly as possible.

Grinding machines also caused loss in moisture and total solids.

A metal strip on the table as close as possible to saws prevents wearing away of the wood at the point where the leather is fed.

ABSTRACTS.

The Heating of Piled Leather. A Tanner. *La Halle aux Cuirs*, Mar. 24, 1918, p. 109. Every spring the writer receives from various persons samples of leather which appear charred and swollen and he is usually asked to try to determine the cause. He points out that fats and oils are readily fermentable and oxidizable, the rate of oxidation increasing with the degree of subdivision of the fat and with rise of temperature. Moreover, oxidation itself is accompanied by a considerable evolution of heat. Now the fats in leather are in an extremely fine state of subdivision and under favorable atmospheric conditions as regards humidity and temperature, such as usually obtain in the spring and autumn, fermentation and oxidation proceed rapidly in leather piles and since the heat cannot escape so rapidly as formed, the temperature rises to such a point as actually to cause the leather to burn. Fermentation with consequent liberation of heat takes place even in unstuffed leathers when piled in a damp condition and sole leather is no exception to this rule. It is wise to keep continuous watch over all leather piles both in the tannery and in the stores in order to guard against this fermentation which may result in serious damage or even in complete destruction. In fact it is dangerous to leave rags, skins, or any porous material impregnated with fat lying around in piles. J. A. W.

* Original paper read at Atlantic City meeting and published in this Journal, June, 1918, pp. 232-239.

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Notes upon Drying. A TANNER. *La Halle aux Cuirs*, Sept. 16, 1917, p. 301. Drying is one of the most important and delicate operations in the production of sole leather, especially by means of rapid tannage. Leather which is allowed to become too dry before stuffing will be difficultly workable, will not absorb the fats readily and will be of lower quality generally. Similarly dried hides never yield a leather as supple and full as do fresh or salted stocks. In fact, if a hide is dried and wet back successively, it finally reaches a stage where it will no longer wet back readily and will not tan at all.

Sole leather dried too much or too rapidly will always be brittle. Drying may induce oxidation of the tannins which will alter the color of the leather. Irregular drying produces marble grain often unjustly attributed to the limes. Yield, quality, and appearance are all modified by the method of drying.

It is well understood that regularity and slowness are two essentials to proper drying. While formerly drying was a tedious operation, modern mechanical devices have overcome much of the trouble, but even these do not prevent too rapid or uneven drying on hot summer days.

A method whose use is continually increasing because of its success when intelligently applied consists in coating the grain before drying with a very small amount of mineral oil. The use of too much oil will lessen the firmness of the leather. This oiling has two advantages: The grain is prevented from drying too rapidly which would render it brittle and it is kept out of contact with the air thus preventing oxidation of the tannins with consequent discoloration. This practice yields a uniform product, good color, and supple grain. The use of pure mineral oils prevents to a certain extent the formation of spew and mold upon the grain.

J. A. W.

Notes upon Drying. A TANNER. *La Halle aux Cuirs*, Oct. 14, 1917. p. 333; cf. preceding abstract. The question has been raised as to the cause of the phenomenon taking place in pelt and leather upon complete drying. The writer admits that he is completely ignorant of this cause. An off-hand explanation might be that when a hide is dried and wet back a great many times it continues to fix certain mineral salts from the water, becoming tanned in a certain sense, thereby losing to a corresponding degree the property of swelling; but this would hardly apply to tanned leather. Leather which has been completely dried before stuffing will always be less supple and will assimilate the fats with greater difficulty than that which has retained sufficient water to preserve its temper.

The writer once performed some experiments in which he dried leather to constant weight in the air, which he calls removing the excess of water, and then completed the drying in a heating device to remove what he terms the water of constitution. On exposing the completely dried leather to air, it always regained some, but never all, of its water of constitution and was always more brittle than leather which had only been air-dried. The conclusion is drawn that complete drying produces

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some internal modification in raw pelt to a large extent and in tanned leather to a lesser but nevertheless appreciable extent and that this renders the grain less supple and increases the difficulties in currying.

J. A. W.

The Acidimetry of Colored Solutions: An Application of the Pocket Spectroscope. ALFRED PINGLE. *J. A. C. S.*, 40, 873 (1918). For detecting the end point in titrating alkaloidal solution containing much coloring matter the author uses a "Beck Thorp" direct vision diffraction, pocket spectroscope, which easily differentiates the color produced by an indicator from that produced by a colored resin. For success it was found that certain precautions were necessary and the conditions were worked out for five indicators.

It was found that the position of an edge of an absorption band produced by an indicator will be determined by the concentration of the indicator, the thickness of the liquid through which the light passes and the degree of alkalinity of the solution.

Two similar titration vessels are used, the shape is not important so long as the same thickness of liquid can be placed between the spectroscope and the light in each. In the first vessel the liquid is brought to such a dilution that a sufficient amount of light can pass through it. The second is used for a blank—in it is placed nearly the same volume of water made alkaline by 1 drop of N/10 NaOH. The indicator to be used is then added slowly from a burette until it is seen that the edges of the absorption bands are sufficiently well defined. The position of the most characteristic edge of the most characteristic band is registered on the scale and is taken as the end point. The volume of indicator is noted and a like volume added to the acid liquor to be titrated, standard alkali is then added until the characteristic absorption band corresponds to that obtained in the blank.

Separate portions of N/10 H_2SO_4 were measured carefully, diluted, and colored with a carefully neutralized vegetable extract to such an extent that an end point could not be distinguished by the unaided eye. They were then given to the experimenter who was not aware of the amount of acid present. The coloring matter used was in some cases prepared from tea and in others from stick licorice. The solutions were titrated against a N/10 NaOH solution which had been standardized in the usual manner. Flat-sided tincture bottles were used for the titrations. All solutions were diluted to approximately 50 cc. at the outset, the thickness of the liquid through which the observations were made being nearly 45 millimeters. Some of the experiments were made by daylight, others at night under such conditions that no end point could have been seen, even had no coloring matter been present.

In all of the experiments given in Table I the coloring matter used was such that the absorption due to it was confined to the blue end of the spectrum. The method can be used equally well when absorption is at the red end. An example of the latter sort is supplied by solutions colored with copper salts.

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TABLE I.—TITRATION WITH DIFFERENT INDICATORS.

Exp. No.	Vol. of N/10 H_2SO_4 by direct measurement cc.	Vol. of N/10H_2SO_4 calculated from titration cc.	Difference cc.	Indicator	Vol. of indicator solution used cc.	Strength of indicator
1	15.0	15.21	+0.21	Cochineal	2.5	Saturated
2	26.0	25.98	—0.02	"	2.5	in 50%
3	20.0	19.96	—0.04	"	2.5	alcohol
4	21.0	21.04	+0.04	Methyl orange	1.0	0.1%
5	17.5	17.49	—0.01	"	1.0	0.1%
6	18.5	19.16	+0.66	"	"	"
7	14.0	14.11	+0.11	"	"	"
8	22.5	22.43	—0.07	"	"	"
9	20.3	20.15	—0.15	Læmoid	0.4	0.2%
10	21.5	21.73	+0.23	"	"	"
11	18.7	18.97	+0.27	"	"	"
12	15.0	14.90	—0.10	Phenolphthalein	0.2	1.0%
13	20.3	20.28	—0.02	"	"	"
14	16.5	16.34	—0.16	"	"	"
15	21.8	21.73	—0.07	Rosolic acid	0.2	1.0%
16	15.1	15.13	+0.03	" "	"	"
17	15.4	15.51	+0.11	" "	"	"

The bad result obtained in Exp. 6 is attributed to a sudden irregularity which developed in the artificial light used as a source of the bright spectrum.

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The characteristics of the indicators used are given—their preparation, concentration and characteristic absorption bands. In the discussion of methyl orange the author states that its spectrum when neutral does not differ from that of the alkaline solution and from this fact contends that the common practice of carrying titrations in which it is used, to "the intermediate tint" is a wrong one. The correct end point has not been reached until no further color change is produced and to further this point gives the following results:

TABLE II.—End Points.

Titration of 25 cc. of N/10 H_2SO_4 with NaOH.

Indicator	Eye alone cc. required	Using spectroscope cc. required
Methyl orange	25.2	25.3
Cochineal	25.3	25.3
Lacmoid	25.3	—

The solutions used were not colored except by the indicator.

The article is summarized as follows:

1. The spectroscope is an efficient means of distinguishing the exact neutral point in many acidimetric titrations.

2. It can be used for this purpose in cases where the unaided eye would fail.

3. The necessary concentration of most indicators is greater when they are used in connection with the spectroscope.

4. The best conditions under which some of the commonest indicators can be used in connection with the spectroscope have been established.

G. W. S.

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CHANGES OF BY-LAWS.

The following changes of the By-Laws of the Association were made effective by a unanimous vote in the balloting, the results of which were announced May 18, 1918.

Section 2 of the By-Laws to be amended as follows:

The objects of this Association are—

(*a*) To devise and perfect methods for the analysis of leathers and all materials used in connection with their manufacture.

(*b*) To promote the advancement of chemistry, especially in regard to its application to problems confronting the leather industries.

(*c*) To publish the results of investigation and research dealing with the above objects.

Sections 7, 8, and 9 of the By-Laws to be amended as follows:

7. The Association shall consist of—

(*a*) Active and Associate members, the latter having all the privileges of the Association except that of voting.

(*b*) Mutual members, who at one and the same time are Active or Associate members of both the American Leather Chemists' Association and the Society of Leather Trades' Chemists. Mutual membership is open to any member of either of the affiliated Associations and shall date from January 1st of the year in which acquired.

8. Every candidate for admission to membership in the American Leather Chemists' Association must be proposed by two or more members according to the form supplied by the Secretary for the purpose. The application, properly filled out, must be sent to the Secretary, who shall lay the same before the Council. If a majority of the Council are in favor of his election, the candidate shall be declared duly elected, and his name entered in the register of the Association.

At whatever period of the year a new member may be elected, he shall be required (unless the Council shall determine otherwise) to pay his dues for that year.

The application blank shall have the following form:

THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

We, the undersigned members of this Association, hereby propose (Candidate's name in full).....as a fit and proper person to become a member of this Association.

Proposed by .....
.....
.....

And I, the said candidate for membership, hereby agree, that if

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elected, I will do my best to support the Association and will observe its By-Laws.

Signature of Candidate.....
Occupation .....
Graduate of .....
Address .....

This application is for Active—Associate Membership.
(Cross out word not needed.)

Extracts from By-Laws.

Section 9.
Section 11.
Section 12.

9. (*a*) Each class "a" member of the American Leather Chemists Association shall pay an annual fee of $5.00 due January 1st of each year and there shall be no entrance fee. In addition to the privileges of the Association, payment of the fee shall entitle the member to the JOURNAL of the Association.

(*b*) Each class "b" member shall pay an annual fee of $7.50—$5.00 of which shall go to the Association of the country in which the member resides and $2.50 of which shall go to the affiliated Association. In addition to all the rights and privileges of the Active or Associated class to which the Mutual member belongs, payment of the annual fee shall entitle such member to the JOURNAL of both Associations.

COUNCIL MEETING.

A meeting of the Council of the A. L. C. A. was held at the Chemists' Club, New York City, July 13, 1918. Messrs. Griffith, Alsop, Reed, Small, Yocum, Rogers, and Smoot were in attendance. Chairmen were appointed for various committees as follows:

Sulphuric Acid in Leather.....J. B. Churchill.
Preparation of Leather Samples for Analysis.....L. E. Stacy.
Extraction of Grease and Oil from Leather.....J. A. Wilson.
Determination of Total, Soluble, and Insoluble Ash in Leather .....J. M. Seltzer.
Sulphite-Cellulose in Synthetic Tans, Tanning Extracts and in Leathers.....C. M. Kernahan.
Practical Uses for Nitre Cake.....J. H. Yocum.
Sulphonated Oil Analysis with Particular Reference to the Hart Modifications.....G. W. Schultz.
Work on Kaolin.....R. W. Frey.
Alternative Filter Paper.....H. C. Reed.
Effect of Hard Water on Tannin.....T. A. Faust.

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The committees on Comparative Analysis, The Testing of Coal Tar Dyes for Leather and The Hydrochloric Acid-Formaldehyde Method were suspended.

The president was instructed to appoint a committee of three to work with the editor of the JOURNAL in order to secure the co-operation of all members in furnishing material for the JOURNAL.

NOTICE OF DELAY IN BINDING.

On account of several unavoidable circumstances there has been considerable delay in securing bound volumes of Volume 12, 1917, of the JOURNAL. The first supply received from the binders has been exhausted and a second supply has not yet arrived. Members are requested not to send in unbound numbers of Volume 12 until notice is given in the JOURNAL of the arrival of a new supply. In the meantime any member who has sent in unbound numbers and has not received a bound volume in exchange can have the unbound numbers returned if such request is made to the manager.

In this connection the manager wishes to call the attention of the members to the issues of which the supply is small and which are advertised on the back inside cover of the JOURNAL. The co-operation of all members is asked in hunting up and sending in any advertised issue, but particularly the issues for January, February and April, 1917.

CORRECTIONS.

On page 322 of the committee report by Mr. J. S. Rogers in Number 7, Volume XIII; Table I, line number 2 should read

Original Leather + 3 per cent. H_2SO_4.

On page 391 of the committee report by Mr. T. G. Greaves in Number 8, Volume XIII; the ninth line and the fourteenth line under Sample W—I, chestnut wood, should read minus.

—0.0050.

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THE EFFECT OF HARD WATER ON TANNINS; COMMITTEE REPORT.*

By T. A. Faust, Chairman.

Last year the Committee did quite a little work on this subject, and when we got all through with it we had not arrived at anything very definite. But there was a pretty strong doubt as to whether there was any considerable destruction of tannin.

As far as laboratory work is concerned, it seemed to indicate that there might be some loss of tannin by a few various chemicals that are found in hard water, but when we proceeded to get practical data to substantiate our laboratory experiments, we were up against it, because all we were able to receive was just opinions. It appeared that no one had any data covering analyses of samples of liquor from tanneries that were using hard water and then subsequently using soft water, but those who had used the two kinds of water thought as far as the actual destruction of tannin was concerned, that there was very little, if any.

Of course, when it came to other matters, such as the color of leather, and the kind of liquors required, and the character of the leather, there was a pretty decided opinion that the hard water gave a rather poor color and not as good a leather, and also stronger liquors were required.

Now I had expected to get considerable data on this very matter by the time of the convention. One of my analytical customers, using hard water for many years, had very complete data as to the amount of liquors required. They turned to artificially soft water, and had expected to let me have by this time the data, using the soft water, but unfortunately they have not used soft water long enough to get data complete, and they have offered to turn this data over to the association for publication. I rather think it is going to be very valuable information, because they have kept very complete records of everything for years, and I rather think we can tell just what difference it does make, not only to the leather and the grain, and the yield of leather, but also as to whether actually a larger amount of tannin is required in one case than the other.

In view of the fact that I was disappointed in getting this

* Read at the Atlantic City meeting of the A. L. C. A., May 18, 1918.

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report, we confined our work this year to a few laboratory tests, making hard waters by the use of various chemicals—That is, we would take distilled water, and make artificially hard water using say, bicarbonate of lime. Another one of the laboratories would take distilled water and use bicarbonate of magnesia, and we have investigated those two salts and also the calcium sulphate and magnesium sulphate, and also common salt.

Now the members of the committee who consented to help me did so at the last minute and got the results in very promptly. I wish to thank them for it, because I rather neglected this work on account of the condition I have mentioned. At the last minute they all jumped in and got the results to me in time for the report. The members of the Committee were Messrs. Alsop, Smoot, Stacy, Blackadder, Kernahan, Seltzer, Marshall and Porter.

Mr. Alsop conducted some work on waters which had been artificially hardened with calcium sulphate and magnesium sulphate, but he found a considerable loss of tannin where extract was diluted with such water and analyzed.

Last year we found the same thing. We found if an extract was diluted with hard water, and then analyzed, it would show a considerable destruction of tannin over the same extract dissolved in distilled water and analyzed. I took the position that that was no indication at all of what happens in a tannery, and I still believe that. As far as the work this year goes, practically everyone found that where the extract was dissolved in any one of these artificially hardened waters, the analysis showed a lower tannin than where distilled water is used in the analysis, but when we came to making up 40° and 50° liquor with hard water, and assumed that these liquors were coming in from some tannery for analysis, a little different result was found, and what few results I want to report here were all on these liquors.

Mr. Porter also found considerable destruction on extract, but he did not have an opportunity to run any liquors.

Mr. Kernahan made up some liquors with calcium sulphate, and he did find a considerable destruction of tannin. I was very much surprised. I hardly expected that. Mr. Smoot and Mr. Stacy ran the same line of work, and they found that calcium sulphate in the water seemed to cause some loss of tannin right in the liquor.

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Another material we examined is bicarbonate of magnesia. That is fairly common in temporary hard waters. Mr. Porter did some work on that, and we did, and we found some very slight destruction; in fact, I think it is within the limits of error, so far as bicarbonate of magnesia goes, I don't think we can prove any loss.

Now when it comes to bicarbonate of lime, which is most important, we unfortunately didn't get one set of results we expected, and, in fact, the only results we had on the bicarbonate of lime we obtained in our laboratory. I am certainly sorry we didn't have more results, because it is an important one.

We found that in the cold there doesn't seem to be any considerable destruction, but possibly long heating may cause some little destruction.

Mr. Seltzer and Mr. Marshall ran tests for common salt. I rather think salt runs a little outside the scope of our work, but Mr. McLaughlin brought up last year a claim that there was some destruction from salt, and I asked Mr. Seltzer to test it and it seems to show some little loss. Of course, few waters have any salt, but there are some waters which do. There is only one thing that I would like to get a few people to say something about, and that is whether they think I am correct in assuming that they cannot depend on the results obtained by diluting an extract with hard water, and analyzing it as such, and whether I have been climbing the wrong tree for two years when I assume the only proper test is to make 40° or 50° liquor and analyze the liquor in the usual way. The reason you get such different results is possibly due to the fact that we have a much higher proportion of calcium and magnesium salts to tannin in the first place than where you make liquors with hard water and subsequently analyze these liquors using distilled water.

The following directions were sent to the members of the Committee:

"The consensus of opinion of the members of last year's Committee indicate that the work this year should be done with waters made artificially hard with various chemicals. Furthermore, there was a belief that it was not practical to do laboratory work on raw materials but that the work should be confined to extracts.

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It is therefore desired to test the effect of the following five chemicals:

Bicarbonate of lime	$CaHCO_3$
Magnesium bicarbonate	$MgHCO_3$
Calcium sulphate	$CaSO_4$
Magnesium sulphate	$MgSO_4$
Sodium chloride	NaCl

In view of the fact that only a few weeks remain before the Convention, the work will be distributed so that each member will only have one of the above five chemicals to investigate. The following procedure is suggested, but each member should determine to his own satisfaction the actual effect of the particular chemical which he is investigating.

SUGGESTED PROCEDURE.

Procedure No. 1.—Add to distilled water sufficient chemical so that an analysis would show approximately 50 part per 100,000 of this particular chemical.

Procedure No. 2.—Dissolve any extract (analysis of which you are making or have recently made) in water prepared as in Number 1, and analyze by the usual method. Report both this analysis and the regular analysis made with distilled water.

Procedure No. 3.—Make a 50 degree Barkometer liquor by dissolving in water prepared according to Number 1 any extract (analysis of which you know) using very little heat. Run a second experiment as above but using distilled water.

Assume that these are two liquors coming in for analysis and analyze in the usual way that you handle liquors, using distilled water in making the dilutions. It will be necessary to re-calculate the tannin to the basis of the original extract.

Procedure No. 4.—Run another set of experiments as in Number 3 but in making the solution, heat to about 140 degrees Fahrenheit for three hours. This is done in order to show the effect of heat where hard waters are used.

From the results obtained above and from any other experiments you may think suitable, give a report as to your opinion of the effect upon tannin, of the presence in water of the particular chemical with which you are working."

The results obtained by the members of the Committee are given in the following tables:

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RESULTS OF PROCEDURE No. 3. (Cold)
All results except A basis original extracts.

Operators		Kind of extract	Nature of H_2O used	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin	
Alsop		Quebracho	Distilled	5.94	5.36	0.58	0.81	4.55	
		Quebracho	Sulphate of lime	6.17	5.62	0.55	0.96	4.66	
	A	Quebracho	Sulphate of magnesia	6.13	5.56	0.57	0.97	4.59	A
		Chestnut	Distilled	10.84	10.32	0.52	3.94	6.38	
		Chestnut	Sulphate of lime	10.94	10.42	0.52	3.98	6.44	
		Chestnut	Sulphate of magnesia	10.94	10.40	0.54	4.04	6.36	
Kernahan		Chestnut	Distilled	40.37	37.75	2.62	11.45	26.30	
		Chestnut	Sulphate of lime	40.37	37.26	3.11	14.63	22.63	
Porter		Chestnut and oak No. 1	Distilled	38.80	37.65	1.15	12.50	25.15	
		Chestnut and oak No. 1	Bicarbonate magnesia	39.00	37.10	1.90	12.10	25.00	
		Chestnut and oak No. 2	Distilled	38.75	37.10	1.65	12.65	24.35	
		Chestnut and oak No. 2	Bicarbonate magnesia	39.50	37.50	2.00	12.40	25.10	
Seltzer & Marshall		Chestnut	Distilled	43.83	40.96	2.87	14.67	26.29	
		Chestnut	Sodium chloride	44.13	41.11	3.02	15.03	26.08	
Smoot & Stacey	A	Chestnut A	Distilled	10.28	10.06	0.22	3.87	6.19	A
		Chestnut A	Sulphate of lime	10.25	9.81	0.39	3.98	5.83	A
Faust & Finch		Hemlock	Distilled	39.93	37.77	2.16	13.50	24.27	
		Hemlock	Bicarbonate magnesia	39.60	37.89	1.71	13 83	24.06	
		Quebracho	Distilled	47.49	45.45	2.04	12.84	32.61	
		Quebracho	Bicarbonate lime	47.61	45.90	1.71	12.72	33.18	

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RESULTS OF PROCEDURE No. 4. (Hot)
All results except A basis of original extracts.

Operators	Kind of extract	Nature of H_2O used	Total solids	Soluble solids	Insolubles	Non-tannn	Tannin	
Alsop	Quebracho	Distilled	6.25	5.59	0.66	0.88	4.71	A
	Quebracho	Sulphate of lime	6.23	5.64	0.59	0.96	4.68	
A	Quebracho	Sulphate of magnesia	6.19	5.66	0.53	0.95	4.71	
	Chestnut	Distilled	11.08	10.60	0.48	4.08	6.52	
	Chestnut	Sulphate of lime	10.98	10.52	0.46	4.02	6.50	
	Chestnut	Sulphate of magnesia	10.90	10.48	0.42	4.04	6.44	
Kernahan	Chestnut	Distilled	40.37	37.80	2.57	11.92	25.88	
	Chestnut	Sulphate of lime	40.37	37.12	3.25	14.72	22.40	
Porter	Chestnut and oak bark No. 1	Distilled	39.05	37.45	1.60	12.50	24.95	
	Chestnut and oak bark No. 1	Bicarbonate magnesia	39.50	37.90	1.60	13.10	24.80	
	Chestnut and oak bark No. 2	Distilled	39.10	37.40	1.70	12.20	25.20	
	Chestnut and oak bark No. 2	Bicarbonate magnesia	39.40	37.90	1.50	12.75	25.15	
Seltzer & Marshall	Chestnut	Distilled	43.38	42.08	1.30	14.84	27.24	
	Chestnut	Sodium Chloride	43.56	42.17	1.39	15.14	27.03	
Faust & Finch	Quebracho	Distilled	46.16	44.46	1.68	13.08	31.38	
	Quebracho	Bicarbonate lime	45.27	43.35	1.92	12.42	30.93	

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RESULTS OF PROCEDURE No. 2.

Operators	Kind of extract	Nature of H_2O used	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin
Alsop	Chestnut	Distilled	51.58	50.72	0.86	17.44	33.28
	Chestnut	Sulphate of lime	54.93	52.44	2.49	23.11	29.33
	Chestnut	Sulphate of magnesia	56.69	55.42	1.47	24.74	30.68
	Quebracho	Distilled	47.58	45.33	2.25	5.58	39 75
	Quebracho	Sulphate of lime	52.07	47.75	4 32	10.89	36.86
	Quebracho	Sulphate of magnesia	53.96	49.66	4.30	12.84	36.82
Kernahan	Chestnut	Distilled	40.37	39.85	0.52	12.01	27.84
	Chestnut	Sulphate of lime	43.34	42.23	1.11	16.07	26.16
Porter	Chestnutoak bark No. 1	Distilled	38.55	37.95	0.60	12.95	25 00
	Chestnutoak bark No. 1	Bicarbonate of magnesia	39.40	38.90	0.50	13 60	25.30
	Chestnutoak bark No. 2	Distilled	39.40	38.80	0.60	12.70	26.10
	Chestnutoak bark No. 2	Bicarbonate of magnesia	40.30	39.60	0.70	14.75	24.85
Seltzer & Marshall	Chestnut No. 1	Distilled	37.84	37.28	0.56	10.46	26.82
	Chestnut No. 1	Sodium chloride	37.80	37.25	0.55	11.63	25.62
	Chestnut No. 2	Distilled	37.36	36.84	0.52	10.74	26.10
	Chestnut No. 2	Sodium chloride	37.41	36.99	0.42	11.16	25.83
	Chestnut No. 3	Distilled	37.39	37.17	0 22	12.40	24 77
	Chestnut No. 3	Sodium chloride	37.38	36.89	0.49	13 49	23.40
	Quebracho	Distilled	46.33	45.52	0.81	10 44	35.08
	Quebracho	Sodium chloride	46.54	45.78	0.76	11.83	33 95
Smoot & Stacey	Chestnut	Distilled	42.78	42.08	0.70	15.04	27.04
	Chestnut	Sulphate of lime	42.28	40.68	1.59	15.36	25.33
Faust & Finch	Hemlock	Distilled	43.76	40.84	2.92	16.87	23.97
	Hemlock	Bicarbonate of magnesia	45.34	44.11	1.23	21.65	22.46
	Quebracho	Distilled	47.96	47.47	0.49	12.97	34.50
	Quebracho	Bicarbonate of magnesia	50.12	49.62	0.52	17.52	32.10
	Hemlock	Distilled	44.59	41.86	2.73	18.08	23.78
	Hemlock	Bicarbonate of lime	46.06	43.68	2.38	21.56	22.12

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DISCUSSION.

MR. WILSON: I would like to ask if the liquor was analyzed in the regular way with hide powder and allowance made for the sodium chloride when that was used.

MR. SELTZER: We ran the experiment using sodium chloride. We added the salt and determined the tannin, and then in calculating our results subtracted the weight of the salt from each residue. We found that the non-tannin was higher in all cases when salt was added to the extract, showing that the presence of salt prevents absorption of tannin by the hide powder.

MR WILSON: As a matter of fact where salt is used in the solution it will penetrate hide fiber, but the concentration of the salt within that hide fiber will be less than that in the solution surrounding it. The result is that you will get increased non-tannins and it will look as though some of the tannin was destroyed, whereas in realty the tannin content may not have been altered at all. I think the methods used in these tests are worthless as a measure of the destruction of tannin. In every case, with every salt that is used, you are going to have a difference of concentration between the outer solution and the liquor which is absorbed by the hide powder. That will be different for every salt and the figures will therefore be practically meaningless.

MR. FAUST: We assumed last year that salt converted tannin into non-tannin. The members of the committee also brought out that temporary hardness seemed to have a solubilizing effect on the insolubles in extracts, therefore decreasing the insolubles and increasing the soluble solids which might compensate for any conversion of tannin into non-tannin by the action of the hard water. I started this work a few years ago expecting to prove ten per cent. loss from hard water, but I could not do it. Last year we found that calcium sulphate seemed to have some action. This year that is the only thing in hard water which we definitely proved to show a loss. There is an actual precipitating action in the use of calcium sulphate. In the case of tanning liquors containing acid, as we brought out last year, there is no destruction until the acid is neutralized.

MR. SMALL: In the case of these reports, Mr. Faust spoke about, I hope that the data he submits will include careful analy-

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sis of both the hard water and the soft water, because the majority of the water softening processes leave the full equivalent in the water of the salts that were originally present.

MR. OBERFELL: I ran some experiments one time, using distilled water, water of moderate hardness and the same water after it had been softened by the permutit system. I was unable to detect any difference in results using these three waters either in dissolving extracts or in dissolving barks. I do not consider my experiments exhaustive enough to say that artificially softened water would be safe in manufacturing extract but I believe it would.

THE PROFITABLE RECOVERY OF PROTEIDS FROM TANNERY WASTE WATERS.*

By C. Lee Peck.

OUTLINE.

- PROFITABLE RECOVERY OF PROTEIDS FROM TANNERY SEWAGE BY THE DORR PROCESS.
  - 1—Definition and Classification of Waste waters.
    - 1. Source of data.
    - 2. Cleansing process Wastes.
      - 1. Soak
      - 2. Hide Mill
      - 3. Beam
      - 4. Water Bate
    - 3. Tanning Process Wastes.
      - 1. Color Wheel
      - 2. Handlers
      - 3. Yard
      - 4. Bleach
      - 5. Scrub House
  - 2. Method of Treatment
    1. Screening.
    2. Sedimentation of lime liquors.
    3. Storage of tanning process wastes.
    4. Concurrent discharges of lime and tanning liquors to reaction tank.
    5. Precipitation of proteids and their sedimentation with the undissolved hide substance.
    6. Drying and marketing proteid sludge.
  - 3. Machinery and Appliances used. Costs of Plant and Operation.
    1. The Harden Screen.
    2. The Dorr Thickener.
    3. Flow Sheet
    4. Estimated costs of 400 to 4,000 side tanneries.
    5. Value of sludge produced.

DIGEST OF RESULTS OBTAINED FROM PROCTOR-ELLISON SEWAGE TREATMENT TESTS FOR MONTH OF MAY, 1917.

I.—One square foot of settling area recovered 81.6 per cent. of the suspended solids from 132 gallons raw sewage daily. The effluent containing 163 parts per million of suspended solids.

II—One square foot settling area recovered 90.42 per cent. of the suspended solids from 86 gallons raw sewage daily, the effluent containing 158 parts per million of suspended solids.

* Read at the Atlantic City meeting of the A. L. C. A., May 17, 1918.

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EFFLUENT.

Analyses following methods of American Public Health Association.

III—The stability of the effluent was 99 per cent.
IV—The reaction was bicarbonate alkaline, averaging 69 parts per million calculated as $CaCO_3$.
V—The color was 1027.
VI—The odor ranged from faint tan to odorless.
VII—The turbidity was 261.
VIII—Oxygen consumed was 839 parts per million.

SLUDGE.

From each side of Sole Leather.

IX—The volume of sludge recovered was 4.6 gallons.
X—The area of sludge bed required for drying per daily side = 10.8 square feet.
XI—Volume contraction on sludge beds = 6.1.
XII—The weight of dry solids was 1.56 pounds.
The ammonia value at $3.50 per unit was $0.01767.
XIII—The estimated cost of plant for sewage treatment, sludge recovery and drying was $7.50.
XIV—The estimated cost of operation, including amortization, interest and freight of sludge to market and 10 per cent. losses was $0.01.

The data for this article was collected from work done at the tannery of Proctor-Ellison and Company, Elkland, Pa., from April 13, to August 1, 1917.

Three million gallons of the tannery waste waters were treated.

Thirty-seven thousand gallons of sludge were recovered from the liquors. This sludge contained about 14,500 pounds of dry solids.

These dry solids contained 6.47 per cent. nitrogen, calculated as ammonia. The Swift Company has quoted the Proctor-Ellison Company a price of $3.50 per unit of ammonia, or a net price of $19.32 per ton at the tannery.

The returns to the tanner in the salvage of this sludge would be about twice the cost of operating the necessary sewage treatment works.

COMPOSITION OF THE WASTE WATERS.

The waste waters produced in the manufacture of leather may be divided into two classes.

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1. Waters resulting from the cleansing processes by which the hide or skin is prepared for tanning.
2. The liquors which are wasted from the actual tanning and finishing of the leather.

The first class, in the aggregate, reacts alkalin; the second class acid. The combined wastes from all processes generally, if not always, react alkalin.

Caustic lime and sodium sulfide are customarily used in the cleansing processes. These materials react with the skins, softening, loosening and dissolving flesh, blood, hair and fat.

This paper is chiefly concerned with the dissolving function of these alkalies; and more particularly with the solvent action exerted upon the proteid substances contained in and attached to the hide. Hide material, flesh, hair and blood are soluble in caustic solutions. They are insoluble in neutral or very diluted acid solutions.

These proteid compounds of lime and soda exist in solutions containing hydrate alkalinity in part at least as colloids. The liquor is milky, viscid, non-settleable and difficult to filter. Lime beam house liquors and the liquors from those subsequent steps which have for their object the removal of lime from the hide are of this character.

Soak, hide mill and other liquors resulting from treatments preceding liming contain proteid substance often in an extremely fine state of division. When these liquors are mixed with the lime wastes, as is the usual practice, solution of proteid substance takes place.

There are the undissolved proteid substances removed in these various cleansing processes also to be considered. Fleshing and unhairing machines produce a larger percentage of fines than the old hand methods. Much of this material finds its way to the sewer.

Those who cure skins for sale to the tanner do not seem to be interested in keeping them free from dirt, which is removed and discharged with the sewage.

The waters themselves which are used in the early stages of hide preparation need not be free from silt and often they are not. This silt also goes into the sewage.

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Quick lime used in the beam house becomes carbonate, insoluble and is periodically discharged.

The lime sludge, contains from one to two per cent. of hair and fleshings.

Lime soaps and sometimes grease are also present, but will not be considered in this paper.

The following are the substances which we desire to segregate and recover:

> Hair, flesh, blood, finely divided hide material in suspension, and proteid substance in solution.

Associated with them as impurities are water, lime in solution and suspension, sundry other calcium compounds in all states as to solubility, lime soap, soda, salt, silt, sand, sulphuretted hydrogen and other noxious gases. This group must be eliminated if the valuable materials are to be made profitable.

Theory of Treatment and Flow Sheet.

The steps by which the desired end may be attained are:

1. Screening: Recovering hair, fleshings and undissolved hide material.
2. Hydraulic classification: Eliminating sand, silt and undissolved lime.
3. Precipitating and recovering the dissolved proteid substance, and settling out the finely divided cellular material, using acid to neutralize. Dissolving and removing lime salts from this precipitate.
4. Preparing the precipitate for market.

1. Screening.—The method of screening hereafter described removes all materials which will not pass a 1/16-inch diameter round opening. This material consists chiefly of hair but contains enough fleshings to render it quickly putrescible in summer. It has a nitrogen content, on a 10 per cent. moisture basis, of 8 per cent. and upwards. It will drain to 55 per cent. or 60 per cent. moisture.

The quantity of material recovered per side of leather will vary widely at different tanneries. It should be artifically dried as fast as recovered.

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II. Hydraulic Classification.—Investigation will probably disclose a wide range in the amount of settleable lime, sand and silt discharged per side of leather manufactured at different tanneries. These materials settle rapidly. On the other hand, hide materials fine enough to pass the screen settle very slowly. By designing the sedimenting basin in such á manner as to cause the liquors to rise as they pass through it and of such dimension that the upward velocity of the liquor is greater than the settling rate of the hide solids, but less than that of the impurities, the latter may be settled out. It is advisable to pass only the strong lime liquors through this unit. Some of the hair and hide solids will settle and be rendered unavailable. The function of this settler being the removal of settleable inorganic materials which would destroy by adulteration the commercial value of the proteid sludge for fertilizer, only liquors containing these materials need be passed through it.

Removal of undissolved lime is essential. The salable sludge to be recovered in later steps must be acid treated. This cannot be profitably done if the sludge contains lime.

The screened and settled cleansing process liquors may then be charged into the reaction tank.

III. Precipitation of the Dissolved Proteids and Recovery of the Precipitate and Undissolved Hide Substance.—Spent tan and other acid liquors are used to neutralize the hydrate alkalinity of the treated cleansing process liquors.

In order that the former may be effectively used for this purpose they are stored and charged from the storage tank along with the alkalin liquors into the reaction tank.

The mixed cleansing process liquors contain, as they come to the reaction tank, very little hydrate alkalinity. The alkalin substances consist chiefly of carbonates and alkalin-organic compounds. The reactions that occur in the reaction tank are to date but little understood.

The ultimate products are: An effluent reacting bicarbonate and containing lime salts in solution; A sludge practically free from lime salts, with the proteids concentrated in a water insoluble and stable condition. These are the properties which render the sludge valuable. In contrast with sludge containing lime, it may be

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dried in the open air and artificially at sterilizing temperatures without considerable loss of nitrogen. It may be digested with a minimum of acid. Its nitrogen content is high enough to render its recovery and preparation for market profitable.

Health authorities of some States will not permit the sale of tannery lime sludge. It has been known to contain disease germs and spores.

The treatment given the proteid sludge by the fertilizer manufacturer sterilizes it.

IV. Preparation of the Proteid Sludge for Sale.—Fertilizer manufacturers will purchase tannery sludge prepared by the methods being described.

The basis on which quotations have been received are:

1. Weight, dried to 10 per cent. moisture.

2. Ammonia units (per cent. per ton) on the total weight of the sludge as received at the factory.

As an illustration:

Let us suppose you have shipped 30,000 pounds of sludge to the fertilizer manufacturer.

As he receives it, it contains 30 per cent. moisture.

The ammonia content, wet basis, is 5 per cent. (5 units).

The price is $3.50 per unit.

The *ammonia basis* would be 5 units.

The weight basis would be: 30,000 pounds less the excess of moisture over 10 per cent. = (30 per cent. — 10 per cent.) = 20 per cent.

30,000 pounds less 20 per cent. = 24,000 pounds = 12 tons= *Weight Basis.*

Then: 12 (tons) × 5 (ammonia units) × 3.50 (price per unit) = $210.00.

Assume that you had dried the sludge to 10 per cent. moisture before shipment. You would have been paid for the same number of tons, but on a different basis as to ammonia as follows:

$$\text{Pounds ammonia} = 30{,}000 \times 0.05 = 1{,}500.$$

$$\text{Per cent. ammonia on 10 per cent. moisture basis} = \frac{1{,}500}{24{,}000} = 6.25$$

You would have been paid

$$12 \times 6.25 \times 3.50 = \$262.50.$$

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That is to say the fertilizer manufacturer has charged $52.50 for evaporating three tons of water. In addition to this you have paid the freight and handling charges.

Sludge cannot be air dried below 25 per cent. to 30 per cent. moisture. It is said to absorb moisture from the atmosphere up to 10 per cent. of its weight.

The sludge as discharged from the reaction tank contains about 95 per cent. moisture.

The problem is to reduce this in the most economical manner to 10 per cent. moisture. The first step, where sufficient area is available, is obviously open air drying.

The proper method and material for preparing open air sludge beds remains a matter for experiment. The bed material should be such that it will not adhere to the dried cake. Meadow land from which the grass has been recently cut would probably serve.

Tan bark and cinders adhere to the cakes. Clean sharp sand might make acceptable beds. All these and such others as may be suggested will be tried at the plants now being erected.

The area required for sludge drying cannot be definitely stated. At the Proctor-Ellison tests the area used was 10 square feet per daily side of leather manufactured. The location of the sludge beds was unfavorable. Ground water level was not more than one foot below the top of the sludge beds. The beds were flooded several times.

Sludge was charged daily for a month. The accumulated cake was dried for another month. The total charge, equivalent to about eighteen inches of fresh sludge, had in that time dried to about three inches. This was firm enough to walk upon or support a loaded wheelbarrow. Shrinkage cracks formed in the process of drying divided the sludge into cakes averaging about 18 inches square. These were stacked on edge against one another to facilitate further drying. Reduction of moisture from 50 per cent. to 30 per cent. is by air drying methods a very slow process under the most favorable conditions.

The sludge cakes should be removed from the beds as soon as they are firm and no longer sticky.

Artificial Drying.—My experience ends at this point. I have

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never attempted to artificially dry tannery sludge on a commercial scale.

The properties of the sludge suggest some points for consideration in this respect. It is an extremely poor conductor of heat. When containing from 60 per cent. to 85 per cent. moisture it has the consistency of butter and will adhere to everything that touches it. Unquestionably it should be dried on beds until it can be handled as a cake. When dried to this point it does not resume its former consistency when wetted.

Plant Design.—Two of the appliances employed in the process may require description. They are the *Revolving Screen* and the *Dorr Thickener.* The revolving screen is a revolving drum which rotates in the conduit through which the liquor to be treated flows. The upstream end of the screen is blind. The conduit is closed at the lower end of the screen. A circular discharge opening in the screen extends through an opening of slightly larger diameter in the partition. The screen is caused to revolve at a peripheral speed of about 75 feet per minute.

The liquor flows from the outside into the drum. The solids are plastered against the outside by the pressure of the inflowing water and are pulled off by the suction of the water which boils up and falls back with the rotation of the drum. It is obvious that the smaller the opening through the screen the better it will operate. On large flows this type may be operated in pairs placed side by side. Arranged thus, they should revolve in opposite directions; the inner being the rising sides, so that the solids fall off between them. A spiral steel conveyor has been suggested as a means for mechanically removing the accumulated solids. Such a unit is being installed at the Peabody plant of the American Glue Company. One square foot of screen will remove solids from liquor flowing at the rate of about 10,000 daily gallons. The power required for screens to treat 2,000,000 daily gallons is about 5 horsepower. Where a single screen is in use the power requirements would not exceed 3 horsepower.

The Dorr Thickener.—The Dorr Thickener is a mechanical device for removing materials which settle from a liquid. It is installed in a circular tank having a flat bottom, or preferably for

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sewage work, sloping at the rate of 1¾ inches to the foot toward the center.

The Dorr Thickener mechanism consists of a central vertical shaft, with radial arms equipped with plows, or scrapers which bring the thickened material to a discharge opening in the bottom of the tank. The thick material is discharged continuously or intermittently as the case may require.

Its power requirements are ¼ horsepower to 2 horsepower the former for a 400 side and the latter for a 4,000 side tannery.

Aside from the questions of economy, the Dorr Thickener is essential to the success of the process.

The Proctor-Ellison Company is treating its sewage by the methods described in this paper, except that at present it is using the conventional form of sedimentation basins.

The sludge produced, when dried, will be salable. It contains two-thirds of one per cent. of lime salts calculated as CaO and four and eighty-six one-hundreths per cent. of ammonia. The ammonia content is 75 per cent. of what was produced from the same sewage treated in the same manner in a Dorr Thickener.

The cost of recovering a unit of sludge is at present upwards of four times what it would be if Dorr Thickeners were used for sedimentation.

The Dorr Thickener affords means for controlling sludge discharge. Loss of ammonia through decomposition of the sludge is prevented by prompt removal as fast as settled to the desired density. The entire bottom of the tank is swept every twelve minutes. Septic nuclei cannot form. Septic conditions in sedimentation are evidenced by rising gases and sludge masses. Plate No. III, p. 9, in bulletin on Tannery Sewage Treatment Tests, shows the surface of a Dorr Thickener which had been treating tannery sewage continuously for two months. It was operating in parallel with a system of fill and draw basins. One of these which had been drained and cleaned within four days, was photographed at the same time as the Dorr Thickener. Plate No. IV in same bulletin shows the sludge cakes which have become septic and have risen to the surface.

Referring now to the flow sheet—Plate No. II.

The cleaning process wastes are collected and caused to flow

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through the Harden screen (Unit No. 1) to the lime sedimentation basin. When waters containing little silt and settleable lime, such as the water bate or hide mill and soaks are being discharged the lime sedimentation unit may be by passed.

The maximum upward velocity through this tank should be about 12 feet per hour and should not exceed 20 feet. Viscosity of the liquors controls the settling rate. Viscosity depends upon concentration of the liquor, the methods of treatment in the lime pits, the duration of treatment, temperature, etc. The dimensions of the tank should, therefore, be calculated from settling tests and volumes of liquor to be treated, and not guessed at.

For installations at 1,000 side tanneries and larger, Dorr Thickeners should be installed in the lime sedimentation basins. Smaller installations might dispense with the Dorr Thickener for this unit, without much increase in cost of operation. The high proportion of lime in this sludge retards putrefaction.

The effluent from Unit 2 is joined with the tan liquors from the storage tank. By means of a float and hose the collected tanning process liquors are caused to be discharged continuously during the period of discharge of the lime liquors.

The composite liquor flows to the reaction tank which is a Dorr Thickener. The diameter of this tank depends upon the rate of flow of liquors to be treated. The maximum recovery of settleable material can be made where the liquor is treated at the rate of about 3.6 gallons per square foot settling surface per hour, or 86 gallons per square foot settling area per day. At this rate, 90 per cent. of the undissolved material may be settled out and recovered. One-half of this settling area would recover about 80 per cent. For reasons other than profit it is generally advisable to provide area sufficient for the most effective sedimentation possible.

Sludge treatment has already been described.

Balance Sheet.

1. *First Cost.*—Cost data are not available. Within a few weeks there will be. Plants under construction and contract at The National Calfskin Company and the American Glue Company at Peabody, Mass., will then be completed.

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Estimated plant cost recently made for treatment works for a 400-side tannery was $20.00 per daily side.

The cost at few plants would be likely to run as high as this.

The estimate for a plant to treat wastes from 4,000 daily sides was $7.50 per side. This includes motors and Ruggles Coles Dryer, the latter costing $7,000.00.

I believe the same rule as to construction costs will apply to operation. A certain amount of supervision is necessary. The gross cost of this for a small plant is not much less than for a large one.

The following estimate of operating expenses applies to the 400-side tannery cited above.

	Per day
Amortization: 20-year period $8,000.00	$1.33
Interest on investment	.84
Labor	1.29
Drying	.53
Power	.50
Freight to market	1.28
Losses	.78
Total cost	$6.55
Selling value of sludge at 6 per cent. ammonia, $3.50 per unit	$7.80
Cost of production	6.55
Profit	$1.25

This is a small profit, a slight drop in the value of the product would wipe it out.

Estimated operating cost for the 4,000-side tannery:

	Per day
Amortization $30,000—20 years of 300 working days	$5.00
Interest on investment	3.15
Sludge salvage	1.20
Sludge drying (Preliminary air $3.00) (Artificial finishing 9.00)	12.00
Delivery to cars	1.50
Freight	11.50
Loss = 10 per cent. =	7.00
Total daily expense	$41.35
Total daily returns—6,600 pounds at $21 =	69.30
Daily profit	$27.95

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Neither of these calculations takes into consideration the material recovered by screening. This is considerable. It is worth about twice as much per pound as the dried sludge. The quantity which could be thus recovered per side varies so widely at different plants that I have not attempted to estimate its value. Both plants are designed to treat an increase of 25 per cent. over the above rating.

In the present state of the art, I would not have the hardihood to recommend sewage treatment for profit, restricting this to sums realized from the sale of products, at least for tanneries manufacturing less than, say, 1,000 sides of leather daily.

Suppression of nuisance, prevention of stream pollution, ending of the state of war or armed truce which in many localities exists between officers of the Commonwealth charged with care of its waters and the tanner, are vastly greater importance.

I do not hesitate to state that this can now be done by methods which will be self supporting.

Just at this time there is another incentive of greater weight than both the foregoing.

It is this last and greatest reason that has impelled me without apology to lay this material before you in its present incomplete condition.

The world is starving. We are at war. Food is ammunition. Our allies look to us. Every pound of fertilizer we can save, this year means a loaf of bread next year. For every side of leather manufactured a loaf of bread is now being wasted.

If the tanneries represented here to-day were equipped to salvage their sludge, the increase to next year's food supply by its use would feed an army division.

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THE NON-TANNIN ENIGMA.

By John Arthur Wilson and Erwin J. Kern.

Probably the most exasperating problem which has disturbed the peace of mind of the leather chemist during the past two decades is that of the accurate determination of non-tannins in vegetable extracts. The literature on this subject was fairly voluminous even before the birth of our Association. The evolution of our present Official Method has made it possible to get concordant results and has thus furnished a satisfactory basis for placing a money value on various tanning materials. In certain classes of research and investigational work, however, mere reproducibility is of no use at all unless the results are accurate or it is at least known whether they are higher or lower than the true value. The questionable assumptions in the Official Method are that the non-tannins are without action upon the hide powder, that all of the water is available as solvent, and that the concentration of non-tannins is uniform throughout all of this solvent. The incorrectness of the first assumption was established by Procter and Blockey[1], who showed that hide powder actually removes from solution considerable amounts of such non-tannins as quinol, gallic acid, and catechin. The present paper is not intended in any manner as a condemnation of the Official Method, for we have nothing better to offer. Nevertheless it has seemed desirable to investigate the source and nature of errors in the hope of gaining a better insight into the mechanism of the method, which may serve as a guide in certain kinds of investigational work in the tannery.

This work was originally inspired by a letter from Mr. W. K. Alsop enclosing results of experiments which he had performed in April, 1910, on the determination of the non-tannins of a chestnut extract made under different conditions as to strength and volume of solution and amount of hide powder used. These results are given in a condensed form in Table I. It is interesting to note first the big variation in results due to varying the amount of hide powder per unit volume of solution and then the comparatively small variation due to altering the concentration while keeping constant the ratio of weight of hide powder to volume of

[1] *J. S. C. I.*, **22**, 482 (1903).

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solution. The highest value is over 20 per cent. greater than the lowest. No tannin was present in any non-tannin filtrate according to the gelatin-salt test.

TABLE I (W. K. Alsop, April 18, 1910).—Showing the Effect of Varying the Proportion of Hide Powder and the Concentration on the Determination of Non-tannin in a Chestnut Extract.

Amount and strength of liquor employed (full strength = 13.5 grams chestnut extract per liter)	Grams wet hide powder used (containing 75 per cent. water)	Per cent. non-tannin found
200 cc. liquor full strength	50	18.76
200 cc. liquor full strength plus 100 cc. water	50	19.40
200 cc. liquor full strength plus 200 cc. water	50	19.69
200 cc. liquor full strength plus 400 cc. water	50	20.73
200 cc. liquor full strength plus 600 cc. water	50	21.95
200 cc. liquor half strength	50	18.50
200 cc. liquor half strength	25	20.20
200 cc. liquor quarter strength	50	18.30
200 cc. liquor quarter strength	12.5	22.07

Further interest in the work was aroused by the report of the Committee on the Effect of Hard Water on Tannins* at the last annual meeting. In many cases the committee found that where an extract was diluted with a weak salt solution, less tannin was found by the Official Method than where pure water was used for dilution. Work on the acid-gelatin equilibrium has shown that this is exactly what one would expect, even though both liquors contained the same amount of tannin and the hide powder removed identical amounts of tannin from each solution. The difference in the determinations is due to the erroneous assumption that the concentration of salt is the same in the solution absorbed by the hide powder as in the surrounding liquor. The committee, however, referred to the difference as indicating a destruction of tannin by the salts. The objection raised to this view by one of us at the time appears not to have been understood, judging from the remarks which followed. It is our further purpose to clear up this misunderstanding.

The molecular mechanism of the process of detannization by the Official Method is extremely complicated and since we are concerned only with the role played by the non-tannins themselves, we have confined our attention to the effects of shaking pure so-

*This issue, page 409.

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lutions of salts and other non-tanning materials with chromed hide powder. Moreover, much work has already been published dealing with the effects of altering the non-tannin contents of actual tanning extracts. The problem thus simplified becomes a series of special cases of the theory of the equilibrium of colloid jellies and electrolytes set forth by Procter and his collaborators. Since all of this work has appeared in the JOURNAL from time to time and is largely of a mathematical nature, we shall not review it here. By examining the mathematical formulas given in the work mentioned, it was found possible to calculate in a rough way the results of all experiments noted below. All results were predicted before any experiments were performed and in no case was disagreement found between theory and experiment. A bare outline of the reasoning employed will be given along with actual results, it being assumed that any sufficiently interested will review and apply the mathematical formulas themselves. The non-tannins are treated separately according to type.

ELECTROLYTES WHICH DO NOT COMBINE WITH HIDE POWDER.

During chroming, the hide powder combines, not only with chrome, but also with sulphuric acid derived from hydrolysis of the chrome alum. Even after thorough washing, much of this acid still remains fixed as ionizable collagen sulphate. In the Official Method it is assumed that the concentration of non-tannins is uniform throughout all of the water of the system. Because of the presence of the sulphate ions from the collagen sulphate, however, any dissolved electrolyte not combining with the hide will become less concentrated in the jelly-phase than in the external solution. The presence of such electrolytes in a liquor, then, will cause too high results for non-tannins and these results must increase as the ratio of weight of hide powder to volume of solution is increased and decrease with increasing concentration of the liquors (both exactly the opposite of what occurs in Alsop's work). A possibility which should be mentioned is that some of the water may be combined with the hide powder and therefore not be available as solvent. In this case, too, the non-tannin figures would be high and increase as the proportion of hide powder employed is increased, but the figures would not be altered

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by change of concentration alone, if this hydration were the only factor causing high results.

Three pure salt solutions were analyzed for non-tannins, just as though they were extracts of analytical strength. The hide powder used was chromed and washed exactly as required by the Official Method. The results of a series of determinations with each salt, using varying proportions of hide powder are given in Table II and indicated graphically in Fig. 2. The effect of varying the concentration is shown for potassium sulphate in Table III and Fig. 1. The values given represent the percentages of non-tannins in the dry salts and would naturally have been 100 per cent. in every case, if all the assumptions in the Official Method were true. The results are, of course, absurd, since a portion of a thing cannot exceed the whole, but the reasoning given above is substantiated. The figures for sodium chloride are higher than they would otherwise have been because of the interaction between the salt and sulphuric acid in the hide powder. In the weakest solution 2 per cent. of total non-tannin residue was found to be sodium sulphate, while in the strongest liquor sodium sulphate constituted 19 per cent. of the total residue. However, if this sodium sulphate be calculated to its equivalent in sodium chloride, it will be found that the results are still high and follow the general rule.

TABLE II.—Showing the Effect of Varying the Proportion of Hide Powder on the Determination of Non-tannin in Various Substances.

Grams of wet hide powder (73 per cent. water) used per 200 cc. of solution	Substance analyzed				
	Gallic acid (used 8.88 grams per liter)	Cane sugar (used 19.7 grams per liter)	Sodium chloride (used 5.86 grams per liter)	Potassium sulphate (used 10 grams per liter)	Magnesium sulphate (used 6.84 grams per liter)
None	100.0	100.0	100.0	100.0	100.0
5	91.8	——	——	100.4	——
6⅔	——	——	100.5	——	100.9
10	86.0	102.6	——	101.1	——
13⅓	——	——	100.8	——	102.8
25	69.6	103.1	——	101.6	——
33⅓	——	——	103.2	——	104.9
50	52.1	104.6	——	103.5	——
66⅔	——	——	107.3	——	107.9
75	43.7	——	——	104.6	——
100	——	——	109.8	——	112.9

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TABLE III.—SHOWING THE EFFECT OF ALTERING THE CONCENTRATION OF LIQUORS ON THE DETERMINATION OF NON-TANNIN. IN EACH CASE 200 CC. OF SOLUTION WERE SHAKEN WITH 47 GRAMS HIDE POWDER CONTAINING 73 PER CENT. WATER.

Gallic acid		Potassium sulphate	
Concentration used (grams per liter)	Per cent. of non-tannin found	Concentration used (grams per liter)	Per cent. of non-tannin found
8.88	54.0	10.00	103.4
4.44	47.1	5.00	103.9
2.22	43.8	2.50	104.9
1.11	40.4	1.25	106.4
		0.63	113.3

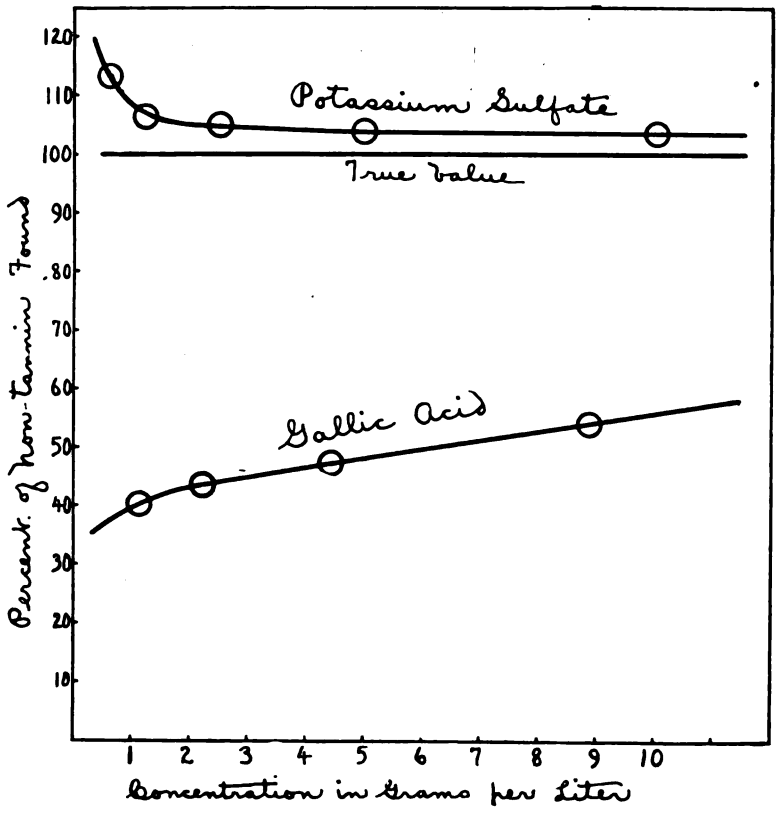

FIG. 1.

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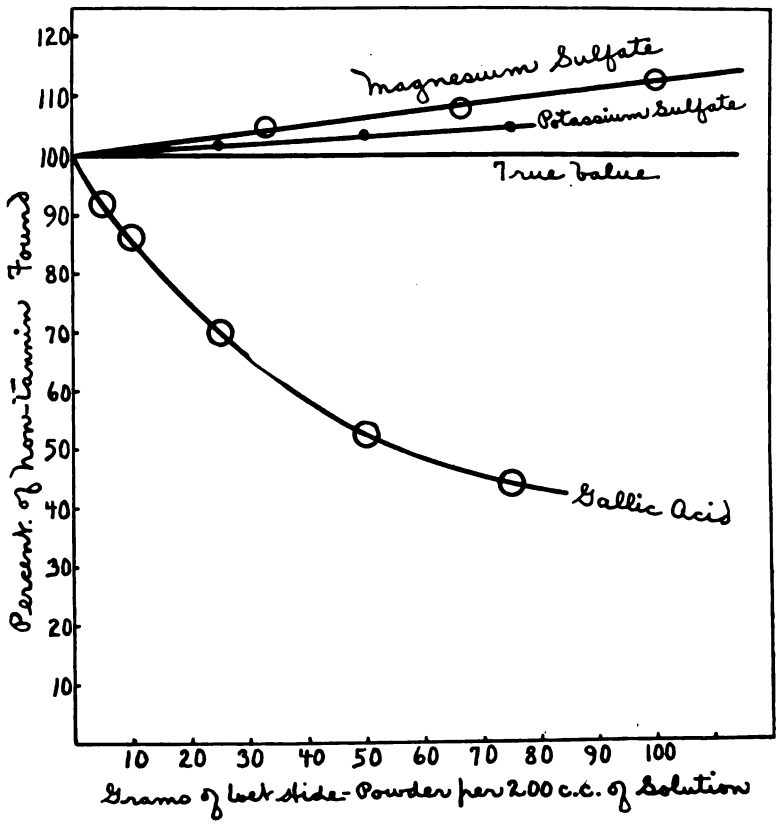

FIG. 2.

It is now plain that, if two identical tanning extracts are taken and to one a salt is added, the liquor containing salt will show less tannin by the Official Method than the pure extract, even though the hide powder removes the same amount of tannin from each solution. The results obtained by the above mentioned committee are in agreement with this, but the conclusion that tannins were destroyed is unwarranted.

Bennett[2] attributes higher non-tannin values produced by the presence of salt to what he calls reduction of the specific surface of the hide powder with consequent lesser adsorption of non-tannins. The above figures furnish no justification for his explanation of the mechanism of the action.

[2] *London Collegium*, p. 52 (1917).

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Non-electrolytes Which Do Not Combine With Hide Powder.

Unfortunately Procter's work has not yet been extended to include non-electrolytes, but such application will probably follow a better understanding of what is known at *thermodynamic environment.* During the preparation of a recent paper on *Collodial Phenomena and the Adsorption Formula*[3], Professor Lamb called the attention of one of us to the fact that proportionality had been assumed between *fugacity* and concentration, an assumption common in chemistry but not necessarily true. Since many readers will probably require further elucidation of this subject, we are taking the liberty of quoting from Washburn's *Principles of Physical Chemistry*[4].

"The tendency of a given molecule to escape from a solution containing it depends upon the conditions which prevail within that particular solution. The molecule is subject to the action of various attractive and repulsive forces as well as to collisions from the molecules which surround it and the sum total of all these environmental influences determines the magnitude of the escaping tendency of the molecule in question. An attempt to analyze further the nature of these environmental influences would in the present state of our knowledge be largely speculative and would have no particular value. It is, however, important to recognize the existence of these influences and their general character, and it will be convenient to have a name to designate the sum total of these effects. The *nature of the medium* surrounding any given molecular species in a solution will, therefore, be called the *thermodynamic environment* of this molecular species."

By the *fugacity* of a molecular species in solution is meant the measure of its tendency to escape from the thermodynamic environment, which surrounds it in the solution, into that condition of *zero thermodynamic environment* which prevails in a *perfect* gas. By the molal fugacity of a molecular species is meant the fugacity per mole per liter, and if fugacity were proportional to concentration, the molal fugacity would be constant.

The molal fugacity of an *ion-species* is approximately constant

[3] J. A. and W. H. Wilson, *J. A. C. S.*, **40**, 886 (1918).
[4] McGraw-Hill Book Co. (1915).

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and the disregard of its variation will therefore have but little influence upon the work of Procter and his collaborators where total ionization is assumed. However, it has been found that the molal fugacitiy of neutral molecules increases very rapidly with increasing concentration of ions in the solution, which is known as the *salting-out effect.*

Now Procter's work has shown that the concentration of ions is greater in the jelly-phase than in the external solution and hence any neutral molecules, such as sugar will become more concentrated in the external solution than in the jelly-phase. Consequently, if sugar does not combine with hide powder, its addition to a tan liquor will tend to cause too high results for non-tannins. The results for sugar in Table II seem to corroborate this, although it must be admitted that similar results would be obtained if some of the water were combined with the hide powder and therefore not available as solvent. It is interesting to note also that Procter and Blockey (loc. cit.) obtained similar results in some cases with glucose.

SUBSTANCES WHICH DO COMBINE WITH HIDE POWDER.

For non-tannins which enter into combination with hide powder, one cannot predict whether results will be high or low without having some idea of the extent of such combination, since the uncombined portion will tend to cause high results while the portion removed from solution will naturally lower the non-tannin figure. The results obtained by Procter and Blockey with gallic acid led us to experiment with this substance as a convenient one. Since it is a stronger acid than acetic, it is not surprising to find it combining with hide powder to a very considerable extent. In the analysis of a liquor containing gallic acid, we should expect that the greater the proportion of hide powder used in detannizing, the greater would be the amount of gallic acid removed from solution and consequently the lower the value for non-tannins found. This is confirmed by the results for gallic acid in Table II and Fig. 2. The reasoning is a trifle more complicated when we consider the effect of altering the concentration of a liquor containing the acid, while keeping constant the amount of hide powder used per unit volume of solution in making the analyses. It is none the less clear, however, that the *amount* of acid fixed per unit of hide powder will *increase* continually with

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the concentration, but the *per cent.* of acid fixed will *decrease* with increasing concentration. This distinction is sufficiently important to merit giving an example. Suppose that of 5 grams of acid in solution 3 grams combined with the hide powder. Now, if we doubled the concentration by using 10 grams of acid, a greater amount than before, say 5 grams, would combine with the hide powder, but this is only 50 per cent. of the total, whereas in the weaker solution 60 per cent. was combined. Therefore, where gallic acid is the non-tannin concerned, we should expect the error to decrease as the concentration is increased and this is shown experimentally in Table III and Fig. 1.

Bennett (loc. cit.) has made a number of suggestions intended to improve the method for determining non-tannins, basing his reasoning on experiments with gallic acid. One is to reduce, by about 23 per. cent., the proportion of hide powder used. The curve in Fig. 2 shows that results would then actually be more nearly correct. But the error would still be large and we should reach a steeper point on the curve, making it somewhat more difficult to get concordant results. It is to be questioned whether anything would be gained by the change from the standpoint of buyer and seller in agreeing upon the value of tanning materials.

Another recommendation is that liquors of only half the present strength be used for analysis. On this point we are unable to follow his reasoning, since the curves in Fig. 1 show clearly that the error increases with dilution.

Summary and Discussion.

It has been shown that the addition to a tan liquor of any soluble substance having no action on the hide powder will tend to raise the per cent. of non-tannins obtained by the Official Method to a point higher than its true value. This error is increased by using larger proportions of hide powder and decreased by using more concentrated liquors.

The addition to a liquor of any soluble non-tanning substance which combines to a very appreciable extent with hide powder, like gallic acid, will tend to decrease the non-tannin figure to a point lower than its true value. This error likewise is increased by using larger proportions of hide powder and is decreased by using more concentrated liquors.

Since lessening the proportion of hide powder reduces the error

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in either case noted above, we have a means of determining whether the non-tannin figure in any case is higher or lower than the true value. In Alsop's experiments (Table I), decreasing the concentration to quarter strength lowered the non-tannin figure only from 18.76 to 18.30, which difference might even be attributed to experimental error. But decreasing the amount of hide powder used from 50.0 to 12.5 grams raised the per cent. of non-tannins from 18.30 to 22.07, showing unmistakably that his non-tannin figures are all lower than the true value and that his liquors contain non-tannins capable of combining with hide powder. A close approximation of the true non-tannin value might be obtained with some tan liquors by plotting values as in Fig. 2 and noting at about what point the curve would cross the axis of ordinates, which point would represent the true value. Of course sufficient hide powder would have to be used in every case to combine with practically all of the tannin.

It should be emphasized in closing that in a liquor of definite tannin content, an alteration of the nature or concentration of non-tannins will cause a corresponding change in the per cent. of tannins obtained by the Official Method, even though there actually is no alteration in the tannin content nor in the amount of tannin removed from solution by the hide powder. It is therefore not permissible in investigational work to compare the tannin figures of liquors containing different kinds or amounts of non-tannins without taking this into consideration.

NOTES ON THE PROCTER-HIRST TEST FOR SULPHITE CELLULOSE.

The editor is in receipt of the following communication:

DEAR SIR:

Messrs. J. H. Yocum and E. S. Nelson (this JOUR., Vol. XIII, No. 5, 204) express their doubt as to the reliability of the Procter-Hirst reaction of sulphite-cellulose, or wood-pulp.

May I, through the JOURNAL, be permitted to draw the above authors' attention to the Appelius-Schmidt reaction (*Ledertechnische Rundschau*, 1914, 29), of which I give an abstract below? And may I also add that, whilst working at Freiberg under Mr. Appelius, we repeatedly found that chestnut extract—although not in every case—gave a precipitate with aniline-hydrochloric acid, whereas, in the absence of wood-pulp, no precipitate was given with cinchonine-hydrochloric acid, as described in the abstract (*Collegium* (London), 1916, No. 12).

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A method by Dr. Möller (*Ledertechnische Rdsch.*, 1914, 11)—extracting the leather with dilute (2 per cent.) NaOH, and subsequent test with aniline-hydrochloride—depends ultimately upon the Procter-Hirst test, and thus leaves considerable doubt as to its reliability. Lauffmann (*Ledertech. Rdsch.*, 1914, 51-52) has tested all three methods thoroughly and favors the Appelius-Schmidt method.

Whatever be the cause of the precipitate forming, whatever test is used, the essential point is to get a method which does not fail, positively or negatively. Such, I believe, is to be found in the Appelius-Schmidt test, which I take the liberty of submitting to Messrs. Yocum and Nelson.

Believe me, dear Sir,

Yours faithfully,

FINI ENNA,
17, Church Walk, Ulverston, Lancs.

Detection of Wood-Pulp in Extracts and Leathers. W. APPELIUS and R. SCHMIDT. *Ledert. Rdsch.*, 1914, 29; abstract *Collegium* (London), 1916; abstracted this JOURNAL, 1914, 566. 1. *Preparation of the Cinchone Solution.*—Mix in a graduated liter flask 5 grams cinchonine (Kahlbaum) with 100 cc. of water and add, drop by drop, concentrated sulphuric acid until a clear solution is obtained. Fill up to the mark and shake well.

2. *Test.*—One hundred cc. tannin solution of analytical strength (filtration unnecessary) is boiled a short time with 5 cc. 25 per cent. hydrochloric acid. The solution is then cooled and filtered if not clear. Fifty cc. of the clear filtrate is placed in an Erlenmeyer flask, and 20 cc. of above cinchonine solution added *without shaking.* If a precipitate forms it is either from (*a*) a catechol tannin, or (*b*) wood-pulp. If no wood-pulp is present the precipitate will be redissolved on heating the mixture to boiling point, without any shaking. If the greyish-white precipitate, due to wood-pulp is formed, it will be quite bulky and form a blackish-brown lumpy mass.

Differentiation of Neradol D and Wood-Pulp.—Five grams paranitraniline are placed in a graduated 500 cc. flask with 25 cc. water and 6 cc. concentrated sulphuric acid. Shake well and add 100 cc. water and 3 grams sodium nitrite in 25 cc. water. Fill up to the mark and do not expose to light. Fifty cc. tannin solution and 15 cc. of above solution are mixed, and if not clear, filtered. Add excess of sodium hydrate to the filtrate. In presence of Neradol D, the solution will be colored blood-red. In examining aqueous extracts from leather and other solutions containing only small quantities of Neradol D, it is advisable to pour the solution (*i. e.*, the mixture of tannin solution and diazo solution) on to filter paper and, after drying, to place a drop of sodium hydrate on the paper. According to the quantity of Neradol D present, a red-rimmed or dark-brown spot will become visible.

The Detection of Wood-Pulp in Leathers is as follows (*Ledertech. Runds.*, 1915, 3): Five to 10 grams of leather is cut into small pieces and extracted once with 100 cc. boiling water. After filtration 5 cc. 25 per cent. hydrochloric acid is added to the filtrate, and the liquid again

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heated to boiling point and filtered. To the clear filtrate 20 cc. of cinchonine solution, and a little pure tannin solution for each 50 cc. of the aqueous extract are added. The liquid is heated, without shaking, to the boiling point. In the presence of even minute quantities of wood-pulp the typical precipitate is always plentifully formed.

NOTE.—The abstractor has obtained the same results with cinchonine chloride dissolved in concentrated sulphuric acid.

F. E.

BOOK NOTICES.

VAN NOSTRAND'S CHEMICAL ANNUAL, 1918. Fourth Issue. Revised and enlarged. Edited by John C. Olsen. 778 pages, 4⅝ by 7⅛ inches; thin paper, flexible leather binding. Price $3.00.

The fourth issue of this very valuable book has been very thoroughly revised and much enlarged. Molecular weights and factors have been changed to accord with the 1917 table of atomic weights. Physical constants of elements and compounds have been revised in accordance with newer data. New compounds which have come into common use have been added to these tables.

About 48 new tables have been added. They include tables replacing older tables, tables on the properties of the elements, tables bearing on calibration and the true volume of glass vessels, the use of indicators, the properties of oils, alloys, glass, etc., specific gravity tables, vapor pressure, units of weights and measures, the capacity of tanks, conversion of units of heat, electricity, temperature, etc., freezing point mixtures, etc.

The section on Stoichiometry has been revised and explanations of the use of the various tables added. A very complete list of new books has been prepared.

Many of the new tables have been taken from the publications of the Bureau of Standards.

Many eminent chemists have assisted in the revision, a list of whom is given.

As revised the Annual is a remarkably complete laboratory reference book.

It is too bad that its usefulness is impaired by the lack of a detailed index. Unless a person is very familiar with the book, much time is often lost in hunting up a desired reference. W. A. F.

SHOE AND LEATHER REPORTER ANNUAL, 1918. Published by the *Shoe and Leather Reporter*, Boston. 734 pages.

An official directory of the shoe and leather industry of the United States and Canada.

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LABORATORY MANUAL of Pfister and Vogel Leather Co. Laboratories, January, 1918. Compiled by Dr. Louis E. Levi, Chief Chemist, and Aug. C. Orthman, Chemist in Charge of Analytical Laboratories, Milwaukee, Wis. Price in U. S. A. $1.10 postpaid.

A handy pocket sized manual containing the methods of analysis used in the laboratories of the P. & V. Leather Co. This includes methods of practically all materials used in leather manufacture either vegetable or mineral.

In addition it contains numerous tables for calculating, etc., and the complete official methods of analysis of the A. L. C. A.

ABSTRACTS.

Tanning Materials of Latin America. THOMAS H. NORTON, Commercial Agent, *Special Agents Bulletin,* No. 165.

INTRODUCTION.

Throughout the more densely populated regions of the earth the available supply of vegetable material for use in tanning is steadily diminishing.

The importance of a more perfect and exact knowledge of the varied substances which contain tannin is now generally recognized.

In not a few tropical and subtropical lands a more or less complete "census" of the trees and shrubs belonging to this category is now being taken.

Few parts of our globe possess such a variety of tannin-bearing plants and trees as those included under the designation "Latin America."

It is the purpose of this study to enumerate and describe as completely as possible the known occurrence of such sources of tannin in the countries in question and to show the extent to which they are already utilized or are easily susceptible of exploitation.

For the sake of convenience these substances may be classified under the following heads: Woods, barks, leaves, excrescences, roots and bulbs, fruits and seeds.

TANNINS FROM WOODS.

QUEBRACHO.

The name "quebracho" is derived from the Portuguese "quebrar," break, and "hacha," ax. Its literal meaning is "ax breaker." Formerly the term was applied to every hardwood tree in South America that dulled the chopper's tools. It is now used commercially in connection with but three trees, the true quebracho, the white quebracho, and the red quebracho. The latter two are of no importance as sources of tannin. Much confusion has resulted from the indiscriminate use of the name for totally different varieties of wood.

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The true quebracho, *Loxopterygium* or *Quebrachia lorentzii* Griseb., belongs to the family of the Awacardiaceæ, or cashew family, and to the genus *Quebrachia.*

It is found in Argentina, Bolivia, Brazil, Paraguay, and Uruguay. The more specific habitat is a district extending eastward some 500 miles from the Andes Mountains, and reaching northward from near the mouth of the Parana River for a distance of about 600 miles. The area of this district is, roughly, 300,000 square miles. The territory in which the tree is industrially exploited includes the northern portion of Argentina and the Province of Chaco in Paraguay.

At the present rate of consumption, it is estimated that the annual cut of quebracho is much less than the sum total of annual growth. The total available supply is estimated at 168,000,000 tons. Less than 1,000,000 tons are cut annually at present.

The quebracho is never found in pure stands. It is scattered through open forests containing, as a rule, a large variety of species. It is rare to encounter more than five quebracho trees per acre.

In consequence of this scattered occurrence, it is necessary to cut annually over about 500,000 acres of forest land in order to secure the quantity required to meet the demands of the world's markets. The value of the quebracho forest land is quite variable. In Argentina, when near a railroad, it commands $2 or more per acre. In Paraguay the average price is $1.50 per acre, although there are cases where the rate is as low as 15 to 25 cents per acre.

The favorable location for the quebracho tree is on slightly elevated ridges lying between water courses. A sandy soil, with moderate atmosphere but abundant soil moisture, seems also conducive to growth.

Where conditions are very favorable, trees are encountered ranging in height from 50 to 75 feet and varying in diameter from 2 to 4 feet. Ordinarily the trees are 18 to 36 feet in height and 18 to 40 inches in diameter. The best wood is found in the virgin forests along the Parana River and the Picole Majo River.

Thus far, the tree seems to be immune against the attacks of insects.

When first felled, the sapwood is of a light yellow color. On exposure to the sun it assumes a light-red tint. The hardwood, when freshly cut, is of a dark, cherry-red color. This deepens with age.

Quebracho wood ranks among the heaviest and hardest woods known. It is the most durable wood found in Argentina. Highly tempered tools are needed to work it, even when in the green state. After complete seasoning it is exceedingly resistant to cutting tools. The specific gravity ranges from 1.27 to 1.38. Ordinarily, 1 cubic foot weighs 78 pounds.

As the quebracho wood is fine-grained and takes a beautiful polish, it possesses a pronounced commercial value and is employed locally for a great variety of uses—for cabinetmaking, house construction, etc. It does not appear, however, that for such purposes it ranks above other hardwoods occurring in Argentina.

Apart from its chief use as a source of tannin, it has been in abun-

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dant demand in Argentina for many years as a satisfactory material for railroad ties. Nine such ties weigh 1 ton. These ties remain on a roadbed indefinitely in a state of perfect preservation. It has been assumed that the large amount of tannin present acts as a preservative and causes the durability. Ties now in use for 25 years are absolutely sound.

Throughout the region of occurrence, the quebracho ties are gradually replacing the iron or steel ties hitherto used in railroad construction. The standard ties on the Argentina broad-gauge railway are 9 feet long, 10 by 13 inches cross section. They cost $2 to $2.50 each. On account of the hardness of the wood spikes can not be driven into it. Holes are therefore bored and bolts are employed to fasten the rails.

The chief drawback to the use of quebracho wood for this purpose is the almost total lack of resilience. There is also a marked tendency to crack when exposed to frost. The necessity of boring holes for the bolts used makes an additional expense.

Experiments have been started in the United States to test the desirability of quebracho ties for our railways. The quebracho timberland of Argentina yields, on an average, 18 ties per acre. American white oak or pine forests yield from 40 to 60 ties per acre.

Tannin Value of Quebracho.

The tannin content of the different parts of the quebracho tree varies somewhat with the region where it grows. Numerous analyses give, ordinarily, the following results:

	Per cent. of tannin
Heartwood	20–24
Sapwood	3– 4
Bark	6– 8

Quebracho extract and wood brought into the United States in 1914 constituted 87 per cent. of all tanning materials imported.

Other Argentine Woods Similar to True Quebracho.

There are several other varieties of forest trees in Argentina and the neighboring territories containing limited amounts of tannins which probably would be utilized as sources of tanning material were it not for the abundance of the true quebracho, with its exceptionally high tannin content. Allusion has already been made to two of these, bearing also the popular designation of "quebracho."

The white quebracho, "quebracho blanco," *Aspidosperma quebracho blanco* (Schlecht), belongs to the family of the Apocynaceæ, which includes common dogbane, or Indian hemp. It is very common wherever the true quebracho occurs. It is found most abundantly in the moister regions of northern Argentina. It is an evergreen tree, conspicuous for its erect stem and wide-spreading crown. The height frequently ranges from 60 to 100 feet, and the diameter ranges from 1 to 3 feet. It is easily distinguished from the true quebracho, as the branches occur nearer the

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ground, and the foliage is much less compact. The wood is strong, hard, and very heavy. The specific gravity varies from 0.88 to 1.1. It is very close grained. The color is yellowish white, with a noticeable pinkish or rosy tint. Although not very durable in contact with soil, it is extensively employed for a variety of forms of woodwork. The dense, compact structure renders it an excellent substitute for boxwood in wood engraving. There is a marked tendency to warp and twist, unless care is taken in the seasoning. Unlike true quebracho, it is subject to insect attack. The wood contains about 3 per cent. of a tannin, which is essentially the same as that found in the true quebracho. The leaves, on the contrary, possess on an average 27.5 per cent. of a tannin, which is almost colorless and is insoluble. The bark contains 4 per cent. of tannin. It is used locally as a febrifuge.

The red quebracho, "quebracho colorado," *Aspidosperma quebracho colorado* (Schlecht), belongs to the same family as the white variety, and occurs in abundance wherever the true quebracho is found. The wood, when freshly cut, possesses a bright red color, which changes to a dark brown with age. It is used for the same purposes as the white variety. Although it is more durable in contact with the soil, its commercial value is less than that of the allied variety. Its tannin content is also quite low.

Other members of the same family share with the above-mentioned varieties the property of hardness, and resemble them in appearance. They are: *Aspidospermum churneum*, with 7 per cent. of tannin; *Aspidosperma peroba*, with 5 per cent.; and *Aspidosperma sessiflora*, with 4 per cent. The wood of the latter contains a pink coloring matter of possible usefulness. It is a tall, stout tree, at present neither well known nor much used. It is found chiefly in Paraguay, in a few localities, north of latitude 26°.

Schinopsis balansae (Engl.), of Paraguay, is reported also to have a fair amount of tannin, and to be used locally.

A member of the sandalwood family, *Iodina rhombifolia* (H. and A.), known as "quebracho flojo" or "sombra de toro," is a handsome evergreen tree, found occasionally in Argentina. Not only the wood, but also the bark, contains fair amounts of tannin.

Machaerium fertile (*Tipuana speciosa*), known as "tipa," contains much the same amount of tannin in both wood and bark.

The wood of *Cedrela tubiflora*, and other varieties of *Cedrela*, occurring in Paraguay, contains sufficient tannin to render it available for tanning purposes. They are members of a comparatively small genus in tropical South America, belonging to the bead-tree family (*Meliaceae*). The trees grow to a large size, and the wood resembles mahogany in appearance.

The wood of young fustic, *Rhus cotinus* (Linn.), which occurs frequently in the West Indian Islands, contains a considerable amount of tannic acid in combination with the glucoside of fisetin, the handsome but somewhat fugitive yellow coloring matter of this tree. No attempt commercially seems to have been made to utilize this source. It is worthy

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of note that cases are very frequent where tannins are accompanied by yellow coloring matters. Young fustic is cultivated to some extent in Italy, where the leaves are encountered in commerce under the designation of Venetian sumac. They are frequently used for tanning purposes throughout southern Europe.

The well-known logwood, *Haematoxylon campechianum* (Linn.), occurring in such abundance in Yucatan, Honduras, San Domingo, and Jamaica, is a similar example of the combination of a dyestuff with tannin. The value of the coloring principle is such that hitherto there has been no attempt made to secure a tannin extract from the wood of this tree.

TANNINS FROM BARKS.

There is a much larger variety of tanning material available in the barks of different trees of Latin America than is the case with the woods. The amount of tannin extracted from quebracho wood alone is, however, much greater than the total obtained at present from all forms of bark, leaves, and roots. Many of these varieties of bark have an extensive local use in the different countries, especially in regions where the quebracho does not occur. Thus far they have not become of marked importance in international trade.

Mangrove Bark.

The only possible exception to the above statement is found in the case of mangrove bark. The export of the bark from Venezuela, and of the extract of the bark from Colombia, have recently become a factor of growing interest in connection with the world's supply of tanning materials.

Hitherto the chief sources of mangrove bark have been Portuguese East Africa, Madagascar, and the East Indies (Celebes, Borneo, etc.). The bark of the mangrove growing naturally in these regions is regarded as distinctly richer in tannin than that found in South America, the content ranging from 38 to 48 per cent.

The mangrove bark of South America comes chiefly from *Rhizophora mangle* (Linn.). Other varieties of *Rhizophora,* as well as of *Ceriops, Avicennia nitida* (black mangrove, or "courouda"), *Avicennia tomentosa* (white mangrove), *Laguncularia, Conocarpus,* and *Cassipourea,* have a certain importance in this connection.

The mangrove jungles of tropical America fringe the tidal estuaries, overrrun soft marshes, and line low, muddy coasts. The trunks and branches emit in abundance adventitious roots which, descending in curves, reach the soil at some distance from the parent stem and give rise to new trunks. The method of expansion closely resembles that of a banyan grove. Another remarkable arrangement of nature for the propagation of the tree is connected with the germination of the seeds. While the fruit is still hanging to the boughs, long radicles emerge from the seeds and descend rapidly to the mud beneath. Here, the plumule

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soon makes its appearance and a new growth is established. Some of the fruits and seeds of mangrove trees are provided with special devices, which enable them to float easily, and to be transported to quite a distance. A novel characteristic is found in the "pneumatophores," or air roots. These are branches of the root proper which project from the mud. They are provided with minute openings, so-called stomata or lenticels, through which air enters, and penetrates, by means of passages in the soft spongy tissue, to the roots spread beneath the surface of the mud.

The wood of some species is hard and durable. The fruit of the *Rhizophora* is sweet and wholesome, and serves to produce a light wine. It has a ruddy brown shell and a delicate white pulp.

The percentage of tannin in the bark of mangrove trees is quite variable, ranging from 5 to 45 per cent. The proportion increases with the age of the tree. The bark encountered in commerce, or used for extraction in the country of origin, contains usually from 22 to 33 per cent.

The tannin present can be isolated in the form of an amorphous, dark-red powder, which so closely resembles in its properties catechu-tannic acid that a possible identity is suspected. In practice, mangrove extract can be substituted with ease for catechu. A reddish-brown coloring matter accompanies this tannin, and imparts to leather a color quite similar to that resulting from the use of hemlock bark.

It is worthy of note that the leaves of mangrove trees are also fairly rich in tannin. They are largely used in the tanneries of southern Brazil. On account of the rapid deterioration in properties during transportation, they are rarely exported. In the tanneries of Santa Catharina, mangrove leaves are the sole material used. The annual consumption is about 400 metric tons. In the two tanneries of Santos there was in 1902 an annual consumption of 1,800 cubic meters of mangrove bark, and of 1,350 metric tons of the leaves. The same year, 1,000 metric tons of bark and 130 tons of the leaves were exported from the port of Santos.

The bark is encountered in commerce in the form of fragments of variable size. It is very hard and very heavy. The cortical cellular tissue has a pronounced reddish-brown tint. For local purposes, the bark or the leaves are used directly by tanneries, and not submitted to extraction. There is now a growing export of mangrove bark, especially from Venezuela. The extraction of the tannin, for convenience and economy in transportation, has not yet been as thoroughly perfected as in the case of quebracho. There are, however, in Colombia, a few well-organized factories for this purpose. One factory at Cartagena, and another at Sinu, 80 miles from the coast, are each capable of producing annually 3,000 metric tons of the solid extract.

The process of manufacturing mangrove extract does not differ materially from that employed in producing quebracho extract. The bark from the younger stems of the tree surrenders its tannin most easily. Care must be taken to avoid the presence of salt, apt to be found on the

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bark, and originating in the salty marshes where the tree grows. The liquors, before concentration, are frequently decolorized, or submitted to the bisulphite process, for the removal of undesirable substances. The solid product obtained by evaporation, in the Colombia factories, contains about 48 per cent. of tannin. It has a vitreous luster and is very brittle. Extracts from mangrove bark of African origin contain from 60 to 70 per cent. of tannin.

Minor Barks.

There are a large number of other barks occurring in Latin America containing varying quantities of tannin, enough to render them at least of local value for the purpose of manufacturing leather. They may most conveniently be treated by grouping them under the countries where each one occurs most abundantly.

Barks of Paraguay.

A very complete exhibit of the barks occurring in Paraguay available for the tanner's use was made at the International Agricultural Exposition, held in 1910 at Buenos Aires. The catalogue of this special exhibit was very full and furnished data of value on each variety exhibited. A well-classified study of this exhibit was published by Dr. W. W. Stockberger in the Journal of the American Leather Chemists Association, 1912, Vol. VII, p. 185.

The following is a résumé of the details given in the above sources, adopting Dr. Stockberger's systematic classification. The native names follow the botanical designation, in parentheses:

Family Anonaceæ.

Rollinia sp. (aratiku gwazu). Tannin content, 4.2 per cent. The tree, well known for its fruit, is very common in the forests, and frequently grows quite tall. The thin bark, abounding in bast fibers, is easily removed.

Family Apocynaceæ.

Aspidosperma polyneuron Muell. (palo rosa). Tannin content, 2.6 per cent. A tall, stout tree yielding excellent timber. It is neither well known nor much used. It is of scattered occurrence in Parana, north of latitude 26°. A pink coloring matter in the wood deserves further investigation. The wood contains also a fair amount of tannin, and mention has been made of it in the preceding section.

Aspidosperma quebracho blanco Schlecht (white quebracho). Tannin content, 4 per cent. This tree has also been mentioned in the preceding section. It is quite abundant in Argentina. The leaves contain 27 per cent. of tannin and the wood 3 per cent.

Family Bignoniaceæ.

Tecoma ipé araliacea (?) (lapacho). Tannin content, 5 per cent. The tree is common and well known and one of those frequently used for timber. The bark is easily removed and has a whitish fracture. The

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epidermis and corky portion are cracked or fissured, and bast fibers are abundant.

FAMILY CÆSALPINIACEÆ.

Apuleia praecox Mart. (yhvihrá-perè). Tannin content, 10.7 per cent. The tree is stout, fairly common, and used for lumber. The pale yellow bark is smooth and not easily removed.

Copaifera lansdorfii Desf. (kupaih). Tannin content, 16.6 per cent. It is accompanied by a certain amount of resinous matter. The tree grows to some size. It is a rare tree except in the forests along the course of the river Monda-ih. The bark is thick and of a ligneous structure. The fracture is whitish-red, and the corky layer readily breaks into small fragments. The fragrant balsam, known in commerce as balsam copaiba, was extracted from this tree at an early date by the Jesuit missionaries.

FAMILY EUPHORBIACEÆ.

Alchornea triplinervia Muell. (tapia gwazu-ih). Tannin content, 11.7 per cent. The tree is abundant and grows to a good size. The bark is quite thick and without bast fibers. Its texture is granulose and fragile. It is easily removed, and has a reddish fracture.

Croton succirubrum (?) (sangre de drago). Tannin content, 11.7 per cent. Resinous matter with a very penetrating odor is present. The tree is small. It is rare in the forests of the uplands but abundant along the rivers. The bark is smooth and easily removed. It is thin, quite fibrous, and has a white fracture.

FAMILY FABACEÆ.

Salbergia sp. (yhsapih-ih). Tannin content, 5.8 per cent. The tree is stout and quite abundant. The bark is smooth and readily removed. It is slightly ligneous and has a blackish fracture.

FAMILY GUTTIFERÆ.

Rheedia brasiliensis Planch & Trianan (pakuri). Tannin content, 21.6 per cent. A small amount of resinous and coloring matters is present. The tree bears fruit, is slender, and attains a height of 40 feet and more. The bark is smooth and easily removed. It is brittle and has a pale-red fracture.

FAMILY LAURACEÆ.

Ocotea sp. (yhvá-ikà). Tannin content, 10.8 per cent. Large amounts of a mucilaginous substance are present. The tree is stout, tall, of frequent occurrence in the forests and often used for lumber. The bark contains few fibers and is grayish when freshly broken.

FAMILY MELIACEÆ.

Cabralea sp. (cancharana). Tannin content, 5 per cent. (in the young bark). The tree attains a good size, is exceedingly abundant, and is occasionally used for lumber. The mature bark is rather thick and somewhat fibrous. It is difficult to remove and has a whitish fracture.

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Cedrela tubiflora (?) (cedro). Tannin content, 12.6 per cent. The tree is largely used for lumber and is common throughout Paraguay. The bark is quite thick, composed of tenuous and fibrous layers superposed. The corky portions are fissured. It is easily removed and has an irregular, reddish fracture.

Two other allied species, containing about the same percentage of tannin in the bark, are also found in Paraguay.

Guarea sp. (guaré). Tannin content, 10.02 per cent. The tree is abundant and of medium size. The bark is easily removed, is ligneous, and has a whitish fracture.

Trichilia catigua A. Juss. (kaátiguá puihtâ). Tannin content, 20.5 per cent. It also contains a large amount of coloring matter. The tree is quite common. The smooth bark is easily removed in strips. It is readily broken and has a dark-orange fracture. The bark is used somewhat for tanning, but gives to the leather an undesirable harshness.

Trichilia hieronymi Griseb. (kaátiguá morôti). Tannin content, 23 per cent. A large amount of a yellow-rose coloring matter is present. The small tree is very common throughout Paraguay. The bark is smooth and readily removed in longitudinal strips. It is easily broken and has a whitish-red fracture. The bark is frequently used locally by tanners and is also employed to dye cotton fabrics.

FAMILY MIMOSACEÆ.

Enterolobium timboüva Mart. (timbo). Tannin content, 22.3 per cent. A certain amount of resinous matter is present. The tree attains a large size, is very common, and is used for lumber. The bark is thick and has a corrugated epidermis and woody bast. The fracture of the young bark is white; that of the mature bark is reddish. It is extensively used by local tanners.

Inga affinis D. C. (inga gwazu). Tannin content, 25.8 per cent. The tree is stout and grows in profusion along the banks of creeks and rivers. The bark is smooth, easily removed from the tree, and deficient in bast fibers. It is brittle and has a whitish-red fracture.

Mimosa sp. (yukeri gwazu). Tannin content, 10.8 per cent. The tree possesses spiny branches and is quite abundant in certain localities. The bark is thick and its fracture is dark yellow. The epidermis is corrugated and quite ligneous.

Peltophorum dubium Taub. (yhvrihrá puihtâ). Tannin content, 31.2 per cent. A very large amount of coloring matter is present. The tree is very common throughout Paraguay and grows at times to an unusually large size. The bark is thick and corrugated and very ligneous. It is easily detached from the trunk in long strips and has a red fracture.

Piptademia rigida Benth. (kurupaih-râ puihtâ). Tannin content, 28.2 per cent. A moderate amount of coloring matter is present. The tree attains a great height and resembles the cedar. The bark is ligneous, the epidermis checked and corrugated. It is easily detached from the trunk and has a pale-rose fracture.

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A very similar species of common occurrence known as kurupaih-râ morôti possesses the same tannin content.

FAMILY MYRTACEÆ.

"Britoa fragrantissima" (?) (yhváviro). Tannin content, 9.2 per cent. This small, fruit-bearing tree is found occasionally in great abundance. The bark is smooth, thin, and easily removed. It is somewhat fibrous and has a whitish fracture.

Campomanesia guavirá (?) (yhvavirá). Tannin content, 11.6 per cent. The tree is fruit bearing and highly esteemed. It is well known and of common occurrence, frequently attaining great size. The bark is thin and fibrous, difficult to remove, and has a whitish-yellow fracture.

Eugenia brasiliensis Lam. (yhvá-poroitih). Tannin content, 43.4 per cent. The wood contains 11.6 per cent. and the leaves 16.6 per cent. There is a certain amount of resin and coloring matter present. The fruit-bearing tree is well known and very abundant. In certain low places it forms dense thickets. It attains a height of 33 feet and a diameter of 18 inches. The bark is smooth and closely adherent to the sapwood, especially when the flow of sap is scanty. It is without bast fibers. Externally it is white. The fracture has the color of hazel nuts.

Eugenia michellii Lam. (nanga pirih gwazu). Tannin content, 28.5 per cent. But little other extractive matter is present. It is very abundant in low grounds, on the banks of small streams. It is apt to be associated with other species of the same genus, quite similar in appearance, and all more or less tanniferous. The bark is thin and smooth, somewhat ligneous, with a whitish fracture.

Eugenia pungens Berg. (yhvá viyu). Tannin content, 10.8 per cent. This is a fruit-bearing tree, quite as well known and highly valued as the yhvá-poroitih. It is larger in size, but of less frequent occurrence. The bark is thin, smooth, and very difficult to remove from the sapwood. The texture is fragile and the fracture has a cinnamon color.

Eugenia sp. (regalito). Tannin content, 15.8 per cent. The tannin is exceptionally pure. The tree reaches a height of about 23 feet. It is less abundant than the allied members of the same genus. The bark is smooth, not very thick, and closely adherent to the sapwood. It is removable in small pieces. The fracture has the color of hazelnuts.

Eugenia sp. (yhvájhay puihtâ gwazu). Tannin content, 28.7 per cent. The tree is not abundant. It reaches 20 inches in diameter and 40 feet in height. The smooth, thin bark is easily removed. It is without bast fibers and has a whitish fracture.

"Myrtus edulis" (?) (yhvá mbopi). Tannin content, 21.8 per cent. The thin, smooth bark is somewhat difficult to remove. It has a whitish fracture.

FAMILY PALMÆ.

Cocos romanzoffiana Cham. (pindo). Tannin content, 6.6 per cent. This palm tree is abundant in all the forests along the coast. It is carelessly destroyed in order to obtain the leaves, which constitute an excel-

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lent forage for draft animals. The bark is often used for tanning the choicer grades of leather.

FAMILY SAPINDACEÆ.

Allophyllus edulis Radlk. (kôkû). Tannin content, 10 per cent. The tree is small and very common. The bark is thin, smooth, and difficult to remove. It is without bast fibers and has a yellowish-white fracture.

Cupania uraguensis H. & A. (kambuatâ). Tannin content, 17.5 per cent. The tree is of moderate size and is frequently encountered in the forests along creeks and rivers. The bark is rather thick and closely adherent to the sapwood. It is removable in small pieces by hammering. It is ligneous and has a reddish fracture.

Cupania vernalis Cambess. (yaguarataih). Tannin content, 15 per cent. The tree is small and fairly abundant. The bark is smooth, somewhat ligneous, and easily removed in large strips. The fracture is of a pale-rose color.

Cupania sp. (cedrillo). Tannin content, 15.8 per cent. The small tree is of scanty development, and is usually found in low places on the banks of creeks and rivers. The thin bark is somewhat adherent to the sapwood. It is fibrous and has a whitish fracture. The natives use it to tan fine skins.

FAMILY SAPOTACEÆ.

Bumelia obtusifolia R. & S. (pihkásurembiu). Tannin content, 8.4 per cent. The tree is somewhat abundant and of moderate size. The smooth bark is easily removed. It is of a slightly ligneous structure.

It will be noticed from the above that Paraguay is unusually rich in varieties of tanniferous barks. A number are of common occurrence and the tannin content is unusually high. In the event, at a later date, of any very acute shortage in the world's supply of tanning materials, the forests of Paraguay alone should be able to contribute notably toward meeting the demands of international commerce.

BARKS OF ARGENTINA.

As already mentioned, the bark of the true quebracho contains from 6 to 8 per cent. of tannin. That of the white quebracho contains 4 per cent. About the same quantity is present in the bark of the red quebracho. Fair amounts of tannin are also present in the barks of other trees, already mentioned in connection with the tannin content of the heart wood, such as "tipa," "quebracho flojo," and varieties of *Cedrela*, all occurring in Argentina.

To these may be added the two trees called popularly "cebil." They occur abundantly in several provinces of Argentina, notably in Salta and Jujuy, remote from quebracho forests, and are extensively used by the tanners of such sections.

Piptademia cebil (Griseb.), red cebil, contains from 15 to 25 per cent. of tannin in the bark and from 6 to 7 per cent. in the leaves.

Acacia cebil (Griseb.) contains 8 to 12 per cent. of tannin in the bark and 7 to 8 per cent. in the leaves.

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Mimosa farinosa (Griseb.). The bark contains 3.9 per cent. of tannin.

Barks of Brazil.

The tree known as Barbatimao (*Stryphnodendron Barbatimao*) occurs in abundance in the State of Minas Geraes, in the south of Brazil. The bark is stated to contain as much as 60 per cent. of tannin. The price at present is $30 per metric ton, laid down in Sao Paulo or Rio de Janeiro. It makes an excellent leather.

The angico tree is found also in Minas Geraes. The bark contains 28 per cent. of a very light-colored tannin, highly valued by tanners. The price at the seaboard is the same as that of Barbatimao.

Remoteness from industrial centers, and the high cost of transportation have hampered any attempt to exploit these barks on an extensive scale.

Eugenia jembos (Linn.) contains 12.4 per cent. of tannin.

The following is a list of the local names of barks found in Brazil, which have a very limited use in tanning: Arica, cannella, garabi, genubata, grannaniamba, guabari, hyrsonima, mimusops, monesia, pimento, santarita, schinus mollis, trumpet-wood, vanigra.

Barks of Chile.

Eucryphia cordifolia Cav. (ulmo). The tree occurs in abundance in Chile. The bark is largely used in local tanneries, and the extract is exported to some extent. This extract is of a dark-red color, and strongly resembles that obtained from mangrove bark. The United States purchases annually a small quantity of this extract, valued at about $8,000.

Persea lingue (lingue). Enormous forests of this tree occur in southern Chile. The reddish-brown, soft bark contains from 20 to 24 per cent. of a tannin, which is very easily extracted by water. It is of extended use locally for the production of the well-known Valdivia leather. It has been used to some extent in Great Britain in tanning leather to serve for uppers.

Laurus peumo. The bark of this tree also serves locally for making upper leather.

Barks of Peru.

The bark of the cascara tree is reported to be in extensive local use for tanning purposes.

The alkaloids present in cinchona bark are largely in combination with quinotannic acid. No attempt has been made to utilize this constituent of Peruvian bark, as far as is known.

Barks of Venezuela.

Tecoma pentaphylla (roble colorado). The bark of this tree contains 27 per cent. of tannin, which is accompanied by a soluble, orange-red coloring matter.

Tecoma leucoxylon (Mart.). This allied variety occurs chiefly in Guiana, where the bark is regularly employed in tanning.

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Weinmannia glabra. The bark has a limited use. The wood of the tree is highly valued for cabinet work.

In addition to the above, the barks of the following Venezuelan trees are occasionally employed by tanners: Aguacate, botoncillo, coco palm, gateodo, simaruba, tamarindo, yagrumo, and urape.

Barks of Mexico and Central America.

Oak bark is widely used for tanning throughout Mexico. The local varieties employed for this purpose are *Quercus xalapensis* (Encinos), *Q. castanea,* and *Q. imbricaria* (laurel oak). The last mentioned is also found in Guatemala and used there for tanning.

Mimosa huamuchil. The bark of this variety of mimosa is widely used, especially in Oaxaca, for making suède leather.

Pithelocolobium dulce (huamuchil o pinzan). The bark is used extensively in Jalisco and Morelos, in tanning saddle and harness leather.

Lysaloma candida (palo blanco). The bark is frequently used.

Acacia malacophylla o mimosa sp. (timbre o timbre). This bark is employed largely to tan leather intended for bookbinding and for shoemakers.

Mimosa biuncifera o acacia sp. (una de gato). In Michoacan, this is used in tanning black goatskins.

Calliandra grandiflora (Raicilla). Employed in Morelos for making soft leathers.

Bursera microphylla (Torote) and *Entorobium cyclocarpum* (Huincastle). The bark of both trees are of a very limited use in Mexico. The latter occurs also in Central America. The pods, as well as the bark, are said to be rich in tannin.

Malpighia punicifolia (nancite or manquitta). The tree is abundant in Nicaragua and in the West Indies. The bark contains from 20 to 30 per cent. of a very light-colored tannin.

Barks of General Occurrence.

Brysonima (Murici).

Stryphnodendron barbatimum (Mort.) (tuga veca). The bark yields the amorphous Barbatimao tannic acid, an amorphous red powder. Both of the above are of scattered occurrence.

Barks of the West Indian Islands.

In the West Indian Islands several trees and vines occur, the barks of which contain tannin in industrial quantities. They may be briefly enumerated in order to complete the geographical survey. They are: *Carapa guianensis* (crab-wood); *spondias lutea* (hay plum); *lecythis ollaria* (kararalli); *mora excelsa* (morá); *cocoloba uvifera* (seaside grape), source of a Kino; *nectandra* (sirnahelli); bloodwood; baromalli or pumpwood; cuyama.

TANNINS FROM LEAVES.

There are but few representatives in this class. Mention has already

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been made of the tannin present in the leaves of the white quebracho of Argentina, and of the extent to which the leaves of mangroves are employed in the tanneries of southern Brazil.

The leaves of yhvá-poroitih, *Eugenia brasiliensis* Lam., so abundant in Paraguay, contain, when air-dried, 16.6 per cent. of tannin. They might advantageously be made the object of systematic annual exploitation, for the purpose of extracting the tanning principle.

Guaiacum arboreum (molle-guayacan). The leaves are locally used for tanning in various tropical regions. The tree is closely allied to *Guaiacum officinale,* the well-known lignum-vitæ.

Sumac, obtained in Mexico from the leaves of *Rhus aromatica* (Ait.) and *Rhus copallina* (Linn.) is the most important member of this category. The dry leaves contain about 13 per cent. of tannin. Mention has already been made of the value of young fustic wood as a source of tannin. The leaves of this tree, *Rhus cotinus,* contain 17 per cent. of tannin. They could also be profitably made the object of a systematic harvesting. These leaves bear easily sea transportation. The different varieties of *Rhus* can advantageously be cultivated, as is now the case in Italy.

The tannin of sumac leaves is very similar to that present in myrobalans, but is somewhat paler in color. It is principally used in the production of light leathers. Sometimes warm sumac liquor is employed to brighten the color of heavy tannages. As a rule, the American varieties are less adapted for making white leather than the Sicilian sumac, on account of the presence of a certain amount of a dark coloring matter. It is to be noted that leather made by the use of sumac tannin is not very resistant to water.

Aspidosperma quebracho blanco (Schlecht). This tree, the "white quebracho" of Argentina, has already been described as having a certain amount of tannin in its wood, *viz.,* 3 per cent. Its bark contains also 4 per cent. The leaves are, however, remarkably rich in tannin, the average amount present reaching 27 per cent. There is probably no other tree occurring abundantly in South America, the leaves of which possess as much value from the tanner's standpoint. No attempt appears to have been made to exploit this source of tannin, probably on account of the great abundance of the true quebracho, side by side with the white quebracho.

In connection with the consideration of the bark of the mangrove, *Rhizophora mangle* (L.), attention has already been directed to the value of the leaves, as rich in tannin, and to their extensive use in the tanneries of southern Brazil.

One of the most interesting occurrences of tannin in the leaves of South American flora is that connected with Paraguay tea, or "yerba de maté." The dried leaves and shoots of *Ilex paraguensis* (A. St. Hil.) are now used by over 30,000,000 inhabitants of South America to make an infusion which, as a beverage, replaces the tea or coffee of other regions.

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The tree is an evergreen, closely related to the holly, and grows abundantly in the mountain forests of Argentina, Paraguay, and southern Brazil. In height it ranges from 15 to 30 feet. The leaves are 4 to 6 inches long, lanceolate, with finely serrated margins.

Infusion is made as in the case of Chinese tea. The so-called maté thus obtained is regarded as having valuable restorative qualities when taken after violent or prolonged physical exercise. It also possesses mildly aperient and diuretic properties. The caffeine present is not much in excess of 1 per cent., as compared with 3.5 to 4.5 per cent. in teas of oriental origin. The physiological action of the tea, therefore, seems to be narcotic rather than stimulative.

The tannin present in the leaves is also much less than in the case of ordinary tea leaves, being on an average about 1.5 per cent. This tannin is very peculiar in character, as it does not precipitate potassio-tartrate of antimony, and is totally without action on hides and skins. Thus far this tannin remains more of a scientific curiosity than an article of commercial interest.

TANNINS FROM ROOTS, BULBS, AND EXCRESCENCES.

This category has also but a very few representatives in Latin America. There are no tannin-bearing excrescences similar to the nut-galls of Syria and China or the knoppern of Austria, and the number of roots is quite small.

Fuchsia macrostemma (churco). The root bark of this Chilean plant contains 25 per cent. of a bright-red tannin. The bark is thin and brittle, and the tannin is easily extracted. It is used locally in Chile for making leather.

Krameria trianria (Ruiz et Pav.) (rhatany). This plant grows in abundance on the slopes of sandy mountains in Peru. The root is woody and branched. The cortex is fibrous, of a reddish-brown color, and is easily separated from the central, reddish-yellow, woody part. It has no smell, but is exceedingly astringent, without being bitter. In commerce it is usually found in the form of powder.

The tannin content ranges from 38.3 to 42.6 per cent. It is much more abundant in the cortex than in the core. In a pure form it is a light yellow powder, quite soluble in water. The extraction by this means is very simple. A certain amount of the concentrated extract is exported. This is not used in tanning alone, but generally as an addition to other liquors. Ruiz, the botanist, was first led to investigate the nature of the root, having noted that it was used by women for rubbing the teeth and strengthening the gums.

Rumex hymenosepalus (Torr.) (canaigre). This plant, known as the sour dock, or wild rhubarb, grows abundantly in those parts of Mexico, seldom visited by rain, where the average temperature is below 20° C. The plant grows to a height of about 3 feet. For centuries the natives of Mexico have used the air-dried, tuberous roots as a material for tanning hides. The name of sour cane (cah na ger) was given the

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plant by the early missionaries, and this was gradually changed into canaigre.

The roots weigh each from ½ up to 2 pounds. They live for five years in the soil. In practice they are gathered when two years old. In commerce canaigre is encountered in the form of reddish disks or as a liquid extract. The plant is cultivated to some extent. It is, in fact, the only tanniferous plant in Latin America which can be profitably made the object of systematic culture.

Tannin is found in all parts of the plant—stalk, leaves, flowers, seeds, and roots—but chiefly in the last mentioned, which greatly resemble dahlia roots in appearance. The percentage of tannin is exceedingly variable, depending upon the conditions of growth. An adverse environment favors a high percentage. On the contrary, in a rich, well irrigated soil the percentage is low. During the annual period of growth the tannin content increases most rapidly at the beginning of summer, when the plant is dying back to the ground. At this period the astringent sap of the leaves retreats into the roots, thus contributing materially to heighten their percentage of tannin. Young roots 3 to 7 inches in length and nearly an inch in thickness contain 10 per cent. of tannin. In roots that are two or three years old the amount present reaches 28 per cent. Trimble states that the pure tannin, which is much like that of mimosa bark, is a yellowish-white powder, readily soluble in water. On boiling with 2 per cent. hydrochloric acid it yields an insoluble, red phlobophane, together with some protocatechuic acid.

The tannin is accompanied by certain red and yellow coloring matters, which are extracted at the same time and distinctly affect the quality of canaigre-tanned leather. When a fresh root is cut the surface blackens on account of the dyestuff present. Canaigre root contains also from 5 to 8 per cent. of starch, which must be removed by some suitable process in order to obtain good results. Hence, when an extract is prepared the temperature is maintained at from 30 to 50° C.

Typical analyses of air-dried roots give:

	Per cent.
Water	14.7
Tannin	27.8–34.9
Non-tannins	9.4–18.1
Ash	1.9– 2.1
Insoluble	33.9
Carbohydrates	6.8

To 100 parts of tannin come 23 parts of carbohydrates.

The dried root and its extract have given very satisfactory results in the tanning of nearly every form of leather. The best results, as regards weight and firmness, are obtained in the finishing of harness leather and in making various light leathers. On account of the easy solubility of the tannin the whole operation of changing hides into leather proceeds with great rapidity. When used alone canaigre imparts to leather a distinctive orange color.

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TANNINS FROM FRUITS AND SEEDS.

This group is more numerous than the two preceding groups, and some of its members are commercially of importance.

Divi-divi.

Cæsalpinia coriaria (Willd.) (divi-divi, also libi-libi). The tannin is found in the seed pods. The tree grows to a height of 20 to 30 feet, and is indigenous in the West Indian Islands, Mexico, Venezuela, and northern Brazil. Its pods are about 3 inches long and ¾ inch broad. They are very thin and smooth. After drying they frequently resemble in shape the letter S. The color is a chestnut brown.

The pods contain from 40 to 45 per cent. of a tannin very similar to that present in valonia. This tannin is most abundant in the tissue of the pod, under the epidermis. There is little in the seeds. A typical analysis of the pods gives the following results:

	Per cent.
Water	13.5
Tannin	41.5
Non-tannins	18.0
Ash	1.6
Insoluble	25.4
Carbohydrates	8.4

To 100 parts tannin come 20.2 parts carbohydrates. The tannin consists of a mixture of ellagitannin and gallotannin. It is accompanied by a considerable amount of oily and mucilaginous matter.

Divi-divi tannin is easily separated in the form of concentrated extract. This latter, as well as the ordinary solutions for tanning purposes, on account of the presence of the above-mentioned foreign matters, are liable to undergo sudden fermentation, especially during electrical storms. In the course of fermentation a deep-red coloring matter is developed, which imparts to leather a dark stain. It is a problem not yet solved how this fermentation may be effectively avoided. The use of ordinary antiseptics has been of some assistance as a preventative.

Divi-divi is an exceedingly cheap source of tannin. Its use is, however, not very extended. As a rule, it is mixed with various barks or their extracts. Leather made by the use of divi-divi extract alone is apt to be firm in dry weather but soft and spongy in damp weather. Ordinarily it is used as a substitute for gambier in the dressing of leather and in the rapid drum-tanning of light leathers. Sometimes its use in connection with leather is simply as a dyestuff.

Divi-divi was first imported from Caracas, in 1769, by Spaniards. By 1848 it had come into widely extended use. The chief ports of shipments are Caracas and Maracaibo.

The name is said to be derived from David Davis, the captain of the first ship to bring to Europe a cargo of the pods.

The present consumption of divi-divi pods in the United States is not large. During the fiscal year ended June 30, 1914, 29,000 pounds were

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imported. The price per pound at the ports of shipment was 1.6 cents. The best known barks are Curacao, Maracaibo, and Monte Christo. Shipments are chiefly from Maracaibo, Parahiba, and Santo Domingo.

The consumption of divi-divi in Germany is much more important. During 1913 the exportation from Colombia amounted to 951 metric tons and from Venezuela to 5,092 tons. The average value per metric ton at the ports of shipment was $4.76.

Caesalpinia tinctoria (H. B. K.; Berth.) (Bogota divi-divi). *Caesalpinia sigyna* (Rottl.) (tari). The pods from these varieties, as well as the so-called "false divi-divi," from other members of *Caesalpinia,* differ but slightly from those of *C. coriaria* in appearance and tannin content, and are occasionally encountered in commerce.

Algarobilla.

Caesalpinia brevifolia (algarobilla; algarobito; algarobo). This plant occurs in sandy, dry regions of northern Chile, and also in Colombia. The pods, which contain three to six seeds, are cylindrical in form, sometimes curved, sometimes straight.

These pods contain from 35 to 53 per cent. of tannin, which is very readily extracted. This tannin appears to be a mixture of ellagitannin and gallotannin. It lies in semiresinous particles adhering loosely to the somewhat open framework of the fiber. It is accompanied by notable amounts of a yellow coloring matter.

A typical analysis is the following:

	Per cent.
Water	13.5
Tannin	43.0
Non-tannins	20.0
Ash	1.6
Insoluble	21.9
Carbohydrates	8.2

To 100 parts tannin come 19 parts of carbohydrates. Concentrated extracts of algarobilla tannin are easily prepared. They are, however, as in the case of divi-divi extract, although to a less degree, somewhat prone to undergo fermentation.

When used in tanning, algarobilla gives much better weight and greater firmness than is the case with divi-divi. It is also less liable to cause discoloraton of the leather. The best grades yield a light-colored liquor, which colors leather but slightly, imparting a light, reddish-yellow tint. After the extract has undergone fermentation it produces a leather of an exceedingly bright color. Experience has shown that it gives inferior results for sole leather and that in general, when employed alone, the leather produced is apt to mold in the sheds. It is, therefore, in almost all cases, blended with other tanning materials, its exceptionally high content serving to strengthen the weaker liquors. It is usually blended with myrobalans, divi-divi, quebracho extract, or hemlock extract. In practically all cases it can replace catechu for blending.

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In consequence of its dyestuff content, algarobilla is occasionally used simply as a coloring material, especially on leather.

Algarobilla is one of the very strongest tanning matters known. There are, however, some closely allied trees in Chile, which yield pods of an even higher tannin content. They are: *Balsamocarpum brevifolium*, 65 per cent. of tannin; *Prosopis pallida*, 60 per cent.; and *Prosopis dulcis*, 62 per cent. They are less abundant, but the pods are held locally in high esteem.

Data on the commercial movement of algarobilla are lacking.

Caesalpinia cacolaco (cascalote). The tree is very abundant in several districts of Mexico, and the pods have formed from time immemorial the chief tanning material of the country. Toluca is the most important point of distribution of the product. Other centers are the towns of Iguala, Morelia, Patzcuaro, Uruapan, and Zitacuaro.

The tannin content is very high. Cascalote has an advantage over divi-divi, in containing a much lower percentage of mucilaginous substances. It gives good results in the manufacture of sole leather, and most other forms of leather, including morocco, glazed kid, box calf, enameled colt, pigskins, etc.

The native method of tanning with the aid of cascalote is exceedingly novel. Prepared hides are first placed for two days in a vat with a "weak" or "sweet" tan liquor, until the hides have uniformly taken the color. They are then removed and sewn up into bags, roughly reproducing the original shape of the animal. These are filled with a stronger tan liquor and a quantity of ground cascolote. The filled hides are then placed in rows on the pavement of the tannery court. The liquor slowly oozes out, and flows into a central pit, whence it is pumped from time to time to refill the hides. The strength of this liquor is retained by new additions of cascalote. The operation continues for about 15 days. For a part of the time the bags are piled upon each other, to the extent of six or eight tiers. The pressure on the lower tiers increases the rate at which the liquor oozes through the hides, and produces a remarkably good tannage. The liquor is finally withdrawn, the sewing ripped out, and the hides are placed in a lay-away vat for a week or longer. They are then ready for the finishing processes.

The consumption of cascalote in Mexico is very great. In the city of Leon, for example, there are 26 tanneries, consuming daily 13,250 pounds of the pods. The price ranges from 3.2 to 3.4 cents per pound. In Mexico City the normal price is $54 per ton. The State of Guerrero supplies annually 500 tons, and the output could be notably increased. There is an unfortunate tendency in some regions to destroy the cascalote trees, in clearing sections for tillage, without seeking to start new plantations in areas less desirable for the needs of agriculture.

There is a certain export of cascalote, but the figures do not appear in American, British, or German statistics.

Paullinia sorbilis (guara). The small tree is found in Brazil and in Colombia. The pods resemble those of cascalote. They contain, how-

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ever, 55 per cent. of tannin. The ground pods are easily extracted, and the liquor is used to make a very light-colored, brownish-yellow leather.

The value of this unusually rich tanniferous fruit has been recognized within the past two years. It may possibly prove to be an important addition to the current supply of tanning agents. (JOURNAL of the American Leather Chemists' Association, 1914, Vol. 9, 214.)

Paullinia cupana (H. B. & K.) (guarana). The seeds contain considerable amounts of both caffein and tannin, and are extensively used in South America for medicinal purposes.

MINOR FRUITS AND SEEDS.

Punica granatum (pomegranate). The fruit rind contains 13.6 per cent. of tannin, resembling closely that of myrobalans. It is accompanied by a considerable amount of starch. The tannin content is most marked in a bitter variety, which is used in preparing morocco leather. The root bark is also rich in tannin.

Inga feuillei (pay-pay). The pods of this Peruvian tree contain 24 per cent. of an almost colorless tannin.

Enterolobium cyclocarpum (Jacq.; Griseb.). The tree occurs in Mexico and Central America. The pods and also the bark are rich in tannin.

Acacia albicans (hiusache, huinacastle). The tree occurs in Mexico. The pods are used as a substitute for gallnuts. Locally the cost is about 10 cents per pound.

Acacia cavenia (espinillo). The tree is encountered in Argentina. The husks of the fruit contain 33 per cent. of tannin.

Guaiacum officinale (lignum-vitæ). The pods are about three-fourths of an inch in length. The seeds possess a leathery pericarp and contain a notable amount of tannin. In Argentina they are used for tanning purposes.

Chrysobalanus icaco. The dried fruits of this Chilean tree resemble closely the myrobalans of India. A large amount of tannin is present in the pulp which surrounds the kernel of the fruit. This latter is about the size of a hazelnut. The tannin content consists of gallotannic and ellagitannic acids. By itself it produces a soft and porous tannage. It is generally used in combination with other dark-colored materials for the production of sole leather and as a cheap substitute for sumac on lighter forms of leather. Thus far the Chilean variety of myrobalans does not appear to have entered into international trade.

Mention finally might be made of the large amount of tannin present in the berries of the coffee tree, *Coffea arabica* (Linn.). The varieties encountered in South and Central America, notably in Brazil, contain 21 per cent. of tannic and caffetannic acids, both in the form of their calcium and magnesium salts. Thus far no attempts have been made to utilize coffee berries as material for tanning. They remain among the potential reserves.

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SUMMARY.

The source of tannin of industrial importance to be found in Latin American countries may be summarized as follows:

Woods	12
Barks	102
Leaves	9
Roots	3
Fruits and seeds	17
Total	143

Should the time ever arrive when southern Africa, Australia, and the Far East are unable to meet the world's demands for the special forms of tanning material, now supplied by them in comparative abundance, there is no question but that the needs of tanners in all countries can be easily and fully met by utilizing the vast and inexhaustible storehouses of tannin, revealed by a careful study of the forest treasures of Latin America.

Analytical Contributions to the Knowledge of Some Vegetable Tanning Materials and Extracts. DR. POLLAK. *Coll.*, 1918, 1-7; *J. S. L. T. C.*, June, 1918. The data in this paper were determined ten years ago and consist of the determinations of the water soluble, acid soluble and insoluble portions of ash of various tanning materials and extracts. The author also estimated CaO and Cl in the water soluble portion and CaO, MgO, Al_2O_3 and F_2O_3 in the portion of ash soluble in acid. The extracts were of different origin, of known purity and method of manufacture. The figures show that mangrove barks contain appreciable quantities of chloride and this fact may be used for detecting mangrove in quebracho extracts, as other writers have pointed out. This method of detection, in conjunction with the higher magnesia content of mangrove, has proved very successful. The method fails in cases where water used for leaching has contained appreciable amounts of chlorine or magnesia, or where salts used for treating quebracho extract have contained those ingredients. The chlorine and magnesia in mangrove bark are due to the cultivation of the trees in sea water. Small quantities of both occur also in malet bark. It is interesting to note the high lime content of mangrove. The ash consists mostly of calcium carbonate and it would seem as if a portion of the mangrove tannin was combined with the lime. This theory would explain many of the characteristics of the mangrove tannage. On concentrating the aqueous extract of the bark, most of the lime separates out as a crust on the sides of the evaporator. The author has determined in what form the lime is combined in leached mangrove bark and finds the following in the dry material:

	Per cent.
Calcium oxalate	6.85
Calcium carbonate	1.48
Calcium sulphate	4.60

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The following tables are abstracts from the originals.

I. TANNING MATERIALS.

			Acqueous extract of ash		Portion of ash soluble in acid	
	Tans	Ash	CaO	Cl	CaO	MgO
Quebracho wood	25.0	1.88	0.05	—	0.69	—
Mangrove bark	34.5	7.34	0.30	0.73	3.15	0.22
Malet	39.9	4.12	0.02	0.18	1.70	0.14
Hemlock	10.5	1.89	0	0	0.45	0.04
Mimosa	36.4	2.17	0	0.08	1.16	0.13
Myrobalans	33.0	2.26	0.01	0	0.20	0.09

II. EXTRACTS.

		Ash	Cl per 100 pts. tannin	MgO per 100 pts. tannin
Pure quebracho (average of 13)		3.20	0.13	0.23
Queb. containing mangrove (average of 11)		2.15	0.93	0.30
Mangrove	Ext.	4.64	2.30	1.23
Myrobalans	Ext.	1.70	0.30	0.29
Mangrove + 25 per cent. myrobs.	Ext.	1.74	1.75	0.58
Malet	Ext.	2.01	0.43	0.36
Mimosa bark with addition of mangrove	Ext.	1.52	1.0	0.35
Chestnut	Ext.	0.45	0	0.20
Pine bark	Ext.	1.40	0.31	0.35
Decolorized sumach	Ext.	3.20	0.36	0.11
Ordinary sumach	Ext.	2.30	0.82	1.07
Mixture of quebr., chestnut, and pine bark extracts.		3.08	0.06	1.00

Leather Dyeing with Natural Coloring Matters. *The Leather World*, March, 1918. Owing to the high cost of aniline dyes at the present time, the writer in this article shows how dyers and stainers can profitably take advantage of the use of natural coloring matters to meet this extra cost and shortage.

ANNATTO.

This coloring matter is obtained from the pulp surrounding the seeds of *Bixa orellana* by crushing. It can be cheaply and successfully employed for staining or dyeing, and is largely used in the Midlands for military work and the pig skin trade. It is not soluble in water, but is dissolved by adding a suitable alkali, such as borax or sodium carbonate, to the water and boiling.

For 1 pound of annatto use 1 ounce of washing soda, or 2 grams of borax, in one quart of water, and boil until all the coloring matter is extracted. It is also soluble in methylated spirit, and is generally bought in this form, although, of course, it is cheaper to make it. One pint of spirit or petrol will dissolve cold 1 pound of annatto.

Annatto finds great favor with curriers, because being either in an al-

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kaline or spirit solution, it will stain greasy leather and produce level results. The well-known "London Color" is practically always obtained by staining with a weak annatto solution.

It can also be usefully employed as a bottom in dyeing greasy or plain chrome leather, and can be used with the borax in the neutralizing of the chrome after tanning, thus performing two operations at once—that is, dyeing and neutralizing at the same time.

The only bad point about annatto is its fugitiveness, and goods stained with it alone will fade in color in so short a time as seven days. A little of an acid yellow, such as tartrazine, should be mixed with it when used for staining.

Turmeric.

This belongs to the ginger family from Asia. The dried and ground rhizemes, or underground stems, are used.

It produces a bright yellow, which is improved by an addition of a small quantity of alum. It can also be used in conjunction with acid colors.

Care should be taken that the liquor is not alkaline, as the color is changed to a reddish brown, but has practically no dyeing power in this form. Unfortunately, turmeric is also fugitive to light.

Weld

is another yellow coloring matter, but is not often used. Other yellow coloring matters are Persian berries, quercitron bark, young fustic, but have practically gone out of commerce.

Fustic

or old fustic, consists of the wood of *Morus tinctoria*, and is still largely used in admixture with logwood to produce a dead black especially in chrome leather in the proportion of one part of fustic to five parts of logwood.

Saffron

obtained from the flower *crocus sativus* is still used in the saddle trade for staining pig skins or hides owing to its good levelling power.

Orchil Paste, Orchil Extract, and Cudbear

are prepared from certain lichens by oxidizing them in the presence of ammonia. It is a substantive color, and can be employed in either a neutral, acid, or alkaline bath. It is still used for dyeing morocco for furniture work, producing a bluish red shade, and is also very useful for "flaming in" or topping. It is not so fast to light or rubbing as a good many dyers think it is.

Brazilwood, Peachwood, and Limawood

are obtained from various species of *Coisalpinia*, but have only a limited application to leather.

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Sanderswood, Camwood, and Barwood.

The best of these is camwood, as it contains about three times as much coloring matter as either sanderswood or barwood. They are used for producing the fawn color on chrome leather for ladies' uppers. Camwood gives the deepest and bluest shade, whilst barwood and sanderswood give yellower and brighter shades.

Cochineal

is very seldom used by the leather dyer, owing to the fact that to produce a bright scarlet it is necessary to use stannous chloride in conjunction with it.

Catechu, or Cutch

is obtained from certain species of acacia growing in India, and is very useful for bottoming when browns are required in that it dyes a level pale brown, and finds favor when skivers for hat-leathers are being dyed. They are first bottomed with the cutch, dyed with chrysoidine, and saddened with potassium bichromate, thus producing a very fast color. It may also be used in the place of logwood in staining blacks, and, if anything, produces a better black.

Logwood

is practically the only natural coloring matter which has not been replaced by aniline dyes. It consists of the heart wood of *Haematoxylin campechianum,* growing in Central America. It is met with in commerce in chips, extract, and hæmatin crystals, and the latter are more generally employed, both in dyeing and staining.

A little alkali is added to the hæmatin when dissolving it, when a better color is observed. The goods are drummed in this solution for about an hour until it is exhausted, and a solution of copperas is run through the axle for a short time, when a bluish black is produced. For a better black one-third of the weight of the logwood is taken of fustic, and it is advisable to add a little copper sulphate to the copperas, as by this means a black is produced which is faster to light than when it is omitted.

Logwood is also largely used for staining blacks, followed by an iron liquor. In all cases after the application of the iron liquor a good washing with water is essential, owing to the bad effect of excess of iron on leather.

Logwood can also be used for producing a pale brown when applied in a slightly acid solution, and is sometimes used in this form in obtaining the well-known London color, being rendered slightly acid by the addition of a little acetic acid.

A good blue can be obtained with logwood if the leather be previously mordanted with alum and cream of tartar, washed lightly, and then dyed with logwood to which has been added a small quantity of chalk. A little bichromate of potash can advantageously be added to the alum bath, producing a faster color.

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Indigo.

This valuable coloring matter is obtained from the leaves of various species of *Indigofera,* and comes almost entirely from India. It possesses practically no direct dyeing power, but under the influence of reducing agents it is converted into indigo white, which is soluble in alkaline solutions, and after the goods have been immersed in this solution for some time, and allowed to oxidize in the air, indigo blue, or indigotin, is produced on the leather. By this means a fast blue is produced.

A much easier method for dyeing with indigo on leather is by treating it with concentrated sulphuric acid, thus producing indigotin-di-sulphonic acid, or indigo extract, which is soluble in water, and can be used in the same manner as an ordinary acid blue dye by the addition of a small quantity of acid. Leather dyed in this manner is not so fast as when the vat method is employed, and the only vat method applicable to leather is the hydrosulphite vat.

The hydrosulphite is made by allowing lime to act upon a concentrated solution of sodium hydrogen-sulphite (sodium bisulphite). The acid sodium hyposulphite produced reduces the indigo to indigo white.

When the vat is in continual use the liquor becomes strongly alkaline, and there is a danger of both the leather and the indigo being injured, and it is advisable to neutralize it by the addition of small quantities of hydrochloric acid. It used to be possible to purchase sodium hydrosulphite before the war in a stable condition, but fortunately it is quite easily made, but the dyeing or reduction must be proceeded with straight away, as the hydrosulphite is very unstable, and liable to oxidation, and in this condition would not reduce the indigo.

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COLOR TESTS OF CHESTNUT BARK.

By T. G. Greaves.

The hope of finding a satisfactory method for the color testing of tanning extracts and the prospects of certain methods being standardized and generally adopted have been the cause of much work and discussion. Whatever may be the opinion of the individual tanner about the way he judges the color of his extracts, it must be admitted that little progress has been made in the standardization of the details or the general adoption of any one method.

In England the colorimeter has been generaly used while in this country the skiver test is the most prevalent. The colori-

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meter has the especial advantage that its results can be numerically expressed, and the extent to which an extract has been decolorized, and the color it will produce on leather, if the customary processes of decolorizing have been used, are capable of mathematical consideration. For this reason, in spite of its sources of error, it is the more definite method of checking the color of extracts on a color specification. The skiver has the advantage that it does not require complicated apparatus or especial care and it gives the tanner an idea of what color he can get on his leather, when compared to a skiver made in the same way from an extract with which he is familiar. The tendency in cases not subject to definite analysis is to make the laboratory tests similar to factory practice. The skiver seems to be the more practical test for almost all purposes.

Although the color of chestnut extract has not been called into question very much between buyer and seller in this country, the recent large exportations to England, where decolorized extract has been generally used and where the color is under close inspection, brings up again the question of color testing and decolorizing.

It has been assumed that an extract of a lighter color than another by one method would be the same by the other method and the considerations leading to the selection of either have been the simplicity of use, the inherent errors, or the definiteness of the idea conveyed. The fact, however, that extracts decolorized by certain processes show very marked improvement of color by the skiver test and very little improvement by the colorimeter test, has been the cause of misunderstanding and shows that the methods are not interchangeable on some kinds of decolorized chestnut extract.

An illustration of the difference that can occur is the effect on the color of leaving the bark of the chestnut tree on or taking it off. The color measurements given were made by the use of the S. & H. colorimeter as modified by G. A. Kerr.* The use of the color solutions eliminated the error which would be incurred in comparing extracts of widely different color with tinted glass. For example, while a No. 2 and No. 1 glass might not match a No. 3 glass, different degrees of color could be matched with

* This JOURNAL, November, 1914, p. 451.

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different column lengths and proportions of the same solutions of the primary colors. Errors which might arise from contamination with iron were avoided by shredding all the bark in a porcelain mortar and breaking up the shreds by hand and shaving the wood samples, of No. 1 and No. 2 in the table, from the split log with broken glass and boring out No. 3, No. 4 and No. 5 with a brass auger bit, made for the purpose, and leaching all the samples in glass. The first three were analyzed and tested for color in duplicate, the duplicates agreeing closely. The color readings are all corrected to a tannin basis to compensate for the differences of strength of solution. The blue is the chief factor in the color grade of a chestnut extract.

	Wood				Bark from same log				
	Condition	Color			Condition		Color		
Log No.		Yellow	Red	Blue	Outer	Inner	Yellow	Red	Blue
1.	Green 32 years old	0.62	2.04	0.41	Fresh	Fresh	4.09	10.87	1.77
2.	Sound seasoned 53 years old	1.07	3.57	0.72	Wormy	Stringy	9.52	24.19	2.72
3.	Half seasoned 40 years old	1.38	4.21	0.71	Sound	Slightly stringy	4.75	15.57	1.69
4.	Half seasoned 60 years old	1.20	4.40	0.61	Wormy	Stringy	4.50	16.60	1.50
5.	Green	1.03	2.60	0.52	Fresh	Fresh	2.81	10.40	0.99

In each case the bark gave a much darker colored solution. The skivers made with chestnut bark, however, are lighter in color than those made from the wood and suggest, in appearance and feel, skivers made from chestnut oak bark. As noted in the committee report (this year) on the Stiasny-Small test, the tannin of chestnut bark, instead of being pyrogallol, like that of the wood is largely catechol. The tannin content of chestnut bark is about seven per cent. (some samples, however, run as high as thirteen per cent.) or seventy per cent. as much as that of the wood.

It is evident, therefore, that the practice of paying more for peeled wood, is only justified (as judged by present methods of testing) when decolorized extract is to be made for the European trade.

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SUGAR IN CHESTNUT EXTRACT.

C. T. Galey and Oscar Riethof.

In the last few years, according to statistics, the use of chestnut extract for the tanning of heavy leather has taken on great proportions, partly on account of the diminishing supply of native barks and their steady advancing price, partly because its merits were well recognized by the tanners. No doubt chestnut extract is a material very well adapted for tanning but complaint is often made that by using a rather high percentage of it in the yard the liquors do not seem to ferment quick enough and so are not producing sufficient acid for the plumping of the stock. It is interesting to note that all brands do not act alike in this respect but that some makes have the reputation of being good acid formers, meanwhile others have a rather low plumping effect, if not used in admixture with other materials which ferment readily.

As far as we know the extent of acid formation in vegetable tan liquors depends mainly on their sugar contents and on the presence of suitable ferments. The writers do not pretend to deal with the second part of the question—the fermenting process, but will confine themselves to the sugars contained in chestnut extract, as these sugars are forming the basic material from which the acids are produced.

It did seem interesting to determine what influence the temperature during leaching has on the sugar contents of chestnut liquors and ultimately extracts. For the experiments we had at our disposal a battery of six autoclaves. On the days tests were carried on the average temperature of the water running onto the tail autoclave was taken by the aid of a recording thermometer, liquor samples were drawn from every take-off and made up into a composite sample which was analyzed as to its tannin and sugar contents. Furthermore a composite sample of the spent wood for the day's run was obtained and subjected to analysis.

It might be mentioned that the loss in temperature of the water running onto the cold dry wood in the head extractor was on the average 28° F., the total loss in water temperature through the whole battery 103°.

The sugar tests were made according to the well known method

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of the American Leather Chemists Association for the determination of sugar in leather. The experiments were carried on with samples taken on thirty-two different days; most of the results were obtained at average temperatures ranging from 240° to 270° F. Where the number of samples was not large enough to give a good average the results were not incorporated in the charts.

The results vary very much for samples taken at the same water temperature on different days, indicating that besides the temperature other factors are influencing the results, chiefly the quality of the wood and other causes which will not be discussed in the present paper. But if the average of a large enough number of tests is obtained, the influence of the disturbing factors is eliminated and the results should show and—as we will see, do show the influence of the temperature.

Table I gives the analysis of the chestnut liquors and spent woods at the different temperatures. To illustrate the great variations obtained at the same temperature on different days, the minimum and maximum figures for the relation of sugar to tannin and non-tannin are tabulated alongside the averages. For better illustration the figures of Table I were incorporated in Charts I and II. In Chart I we want to point to the ascending line of the tannin figure. In as much as the number of gallons taken per cord of wood was the same in all cases, the increase in the percentage of tannin at higher temperature means higher yield. The curve for the purity of spent wood runs in the opposite direction.

It is a well known fact that the extent of leaching chestnut wood in autoclaves cannot be judged, as in open leaching, by the tannin contents of the spent wood because, under the rather high pressure and temperature to which the wood is subjected, cellulose is broken up and becomes soluble during the laboratory extraction. A portion of this converted cellulose is absorbed by the hide powder, but is not what we consider a true tannin. It is, however, an established fact that the purity of the spent wood is a good indicator for the extent of the leaching and the truth of this is shown by our experiments which prove that the lower the purity of the spent wood, the better the leaching.

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TABLE I.

Analysis of Chestnut Liquors Taken at Different Leaching Temperatures.

Temerature Fa.	Total solids	Soluble solids	Insoluble solids	Non-tannins	Tannin	Purity	Glucose	Total sugar	Purity of spent wood	Number of tests	Parts glucose			Parts total sugar			Parts glucose			Parts total sugar		
											To 100 parts tannin						To 100 parts non-tannin					
											aver.	min.	max.	aver.	min.	max.	aver.	min.	max.	aver.	min.	max.
210°	1.87	1.81	0.06	0.73	1.08	57.16	0.091	0.154	62.30	2	8 3	7.8	8.9	14.3	13.6	15.1	12.2	10.5	14.0	20.8	20.3	21.5
220°	2.61	2.56	0.05	1.06	1.50	57.50	0 264	0.515	51.38	1	17.6	—	—	34.3	—	—	25.0	—	—	48.6	—	—
240°	2.41	2.34	0.07	0.90	1.44	60.00	0.182	0.394	48.69	3	11.2	6.7	14.3	24.1	15.4	30.0	18.9	14.6	22.4	40.9	34.0	46.9
250°	2.41	2.35	0.06	0.87	1.47	61 70	0.188	0.395	49.41	6	13.4	10.2	23.4	25.8	16.6	50.9	21.8	17.2	27.5	40.2	31.9	54.6
260°	2.46	2.40	0.06	0.91	1.49	61 20	0.197	0.401	45.63	8	12.9	7.7	19.1	26.3	17.9	38.1	21.1	15.9	25.1	43.1	35 3	50.1
270°	2.53	2.47	0.06	0.96	1.51	60.51	0.222	0.403	39 73	8	14.4	9.4	23.3	29.9	18.0	50.6	22 6	18.9	27.3	46.6	36.0	62.6
280°	2.99	2.94	0.05	1.23	1.71	57.30	0.279	0.596	33.91	2	16.2	14.8	17.7	34.6	29.4	39.9	22.8	22.0	23.6	48.2	48.6	49.6
290°	3.09	3.05	0.04	1.30	1.75	56.50	0.292	0.674	34.10	1	16.7	—	—	38.5	—	—	21.7	—	—	51.8	—	—

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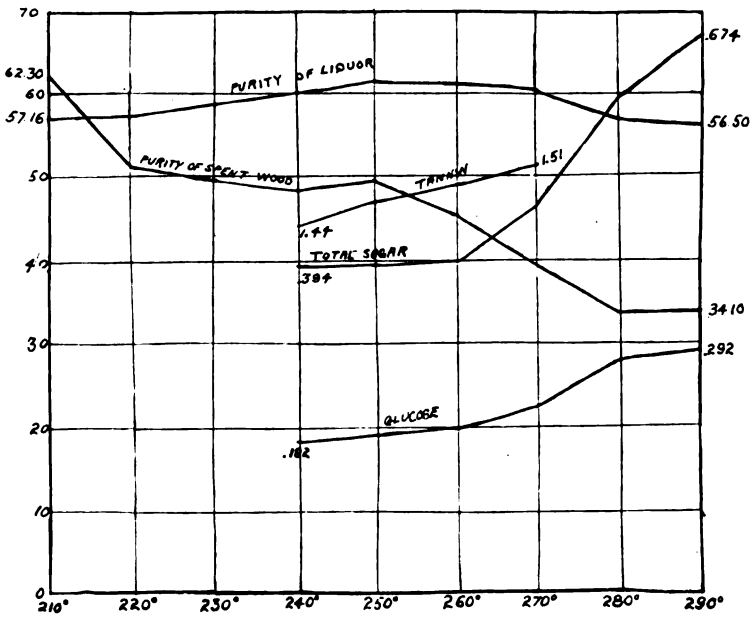
CHART NO. 1



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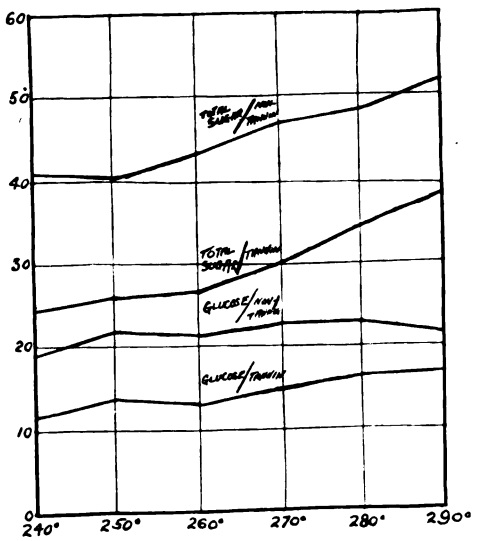

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TABLE II.

ANALYSIS OF DIFFERENT BRANDS OF CHESTNUT EXTRACT.

Open Leaches.

Brand	Total solids	Soluble solids	Insoluble solids	Non-tannins	Tannin	Purity	Glucose	Total sugar	Parts glucose	Parts total sugar	Parts glucose	Parts total sugar
									To 100 parts tannin		To 100 parts non-tannin	
A 1	39.85	38.74	1.11	13.43	25.31	63.51	2.90	4.97	11.46	19.60	21.60	37.01
A 2	40.07	38.69	1.38	13.40	25.29	63.07	2.93	4.96	11.59	19.62	21.87	37.02
A 3	39.34	39.13	0.21	12.97	26.16	66.50	2.92	4.40	11.16	16.82	22.52	33.93
A 4	37.68	37.44	0.24	13.52	23.92	63.45	3.27	5.26	13.67	22.00	24.18	38.90
B 1.....	37.48	36.74	0.74	11.10	25.64	68.37	2.43	4.40	9.48	17.16	21.90	39.64
B 2	37.05	36.67	0.38	10.23	26.44	71.37	1.84	3.86	6.97	14.60	18.00	37.74
C*	35.00	34 98	0.02	9.04	25.94	74.17	1.62	2.69	6.28	10.37	17.92	29.76
D*	37.53	37.50	0.03	10.53	26.97	71.92	1.59	3.10	5.89	11.49	15.10	29 42
Average .						67.80			9.56	16.46	20.39	35.43

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TABLE II.—(Continued)

ANALYSIS OF DIFFERENT BRANDS OF CHESTNUT EXTRACT.

Autoclaves.

Kind	Total solids	Soluble solids	Insoluble solids	Non-tannin	Tannin	Purity	Glucose	Total sugar	Parts glucose	Parts total sugar	Parts glucose	Parts total sugar
									To 100 parts tannin		To 100 parts non-tannin	
E 1	29.22	28.54	0.68	10.28	18.26	62.53	2.68	4.77	14.68	26.12	26.07	46.40
E 2	36.63	35.84	0.79	13.01	22.83	63.77	3.31	5.99	14.50	26.24	25.44	46.04
F 1	92.59	90.60	1.99	31.94	58.66	63.34	8.15	15.73	13.89	26.82	25.52	49.25
F 2*	43.89	42.44	1.45	14.67	27.77	65.43	4.19	8.45	15.11	30.43	28.56	57.60
G 1	35.64	35.35	0.29	9.82	25.53	71.63	1.75	3.91	6.85	15.31	17.82	39.82
G 2*	39.32	38.19	1.13	13.21	24.98	65.42	2.72	6.29	10.90	25.18	20.60	47.61
H*	37.01	36.42	0.59	11.76	24.66	67.71	2.17	5.50	8.80	22.30	18.45	46.77
I*	40.61	38.38	2.23	12.55	25.83	67.30	2.42	4.84	9.37	18.74	19.28	38.56
Average .						65.89			11.76	23.89	22.72	46.51
Method of leaching unknown.												
J*.....	37.91	37.67	0.24	12.59	25.08	66.58	2.80	4.99	11.16	19.90	22.24	39.64
K	37.60	37.20	0.40	11.59	25.67	68.84	2.47	5.08	9.63	19.80	21.31	43.83

* For these results we are indebted to Mr. J. M. Seltzer of the Kistler Leather Co.

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There are some very interesting curves in Chart II. All four curves are ascending with increasing temperature. As could be expected, the lines for the glucose do not vary much but the lines showing the relation of total sugar to tannin and non-tannin are on a steep incline, indicating that under the pressure and high temperature existing during the leaching process cellulose is broken up and partly converted into glucosides which, after inversion, precipitate copper oxide from Fehling's solution.

These results show that it is in the power of the manufacturer of chestnut extract to influence to a certain extent the sugar contents of his produce to suit the requirements of his customer, the tanner. As a rule the heavy leather tanner prefers, for our standard tannages, extracts with a high percentage of sugar. This fact is well taken care of by some extract manufacturers.

In Table II the results are given of analyses of chestnut extracts from eleven plants, some using open leaches, some autoclaves. For two brands the method of leaching is not known to the writers. It can be seen that on the average the sugar contents of the products which are leached in autoclaves is considerably higher than in the extracts made in open leaches. This difference is noticeable especially in the figures showing the relation of total sugar to tannin and non-tannin, but is naturally not so pronounced in the figures for glucose. This confirms our results as given above.

We regret that we were unable to have our tables more complete, especially for some temperatures, but the experiments had to be concluded on account of one of the writers being called to the colors.

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REPORT OF THE COMMITTEE ON STANDARD METHODS OF EXAMINING DISINFECTANTS.* [1]

Section A. Introduction.

In 1912 the Laboratory Section, A. P. H. A., adopted as the official standard method for the examination of disinfectants the procedure devised by Anderson and McClintick[2] with certain modifications relating chiefly to the phenol and the culture media. The committee report stated at that time:

"Since the publication of Bulletin No. 82 comparisons of the results of tests made by different members of the Committee upon duplicate samples have led to the belief that further studies may develop points of value in the further elaboration of the method which will tend to produce greater uniformity of results in the hands of different workers."

During the past two years the Committee on Standard Methods of Examining Disinfectants has been engaged upon such further studies looking toward the improvement of certain recognized defects in the present standard method.

Of the present membership only three have been in a position to do actual laboratory work. The Committee has been fortunate, therefore, in having secured the collaboration of Dr. Wilhelm Dreyfus, of the Chemical Department of the West Disinfecting Company, of Dr. E. M. Houghton, of the Park, Davis Research Laboratories, and of Mr. J. M. Weiss of the Research Department of the Barrett Manufacturing Company. It was therefore possible to arrange for the participation of the following laboratories in the comparative tests:—the Hygenic Laboratory of the U. S. Public Health Service, the laboratory of the Bureau of Animal Industry on behalf of the Federal Insecticide Board, the Lederle Laboratories on behalf of the West Disinfecting Company, and the Laboratories of Parke, Davis & Co., and the Barrett Manufacturing Company. Mr. J. H. Wright of the Lederle Laboratories has been in part responsible for that

* A. J. P. H., 1918, pp. 506-521.

[1] This report was presented before the Laboratory Section of the A. P. H. A., October 20, 1917, and was accepted and ordered published, in order that it might come up for final adoption at the next meeting. Pending such final adoption it is not official.

[2] Anderson and McClintick, Hyg. Lab. Bull. No. 82, 1912.

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Laboratory's contribution and has in addition made the special studies of the effect of acidity in media.

Investigations by the Committee.

Early in 1915 a comparative test was arranged whereby each of the five laboratories underook to test two special disinfectants by both the R-W and H-L procedures and by two techniques under each procedure, making eight tests in all. Each test was done in triplicate to obtain data upon the reliability of the various procedures. The first technique employed the ordinary phenol and organism used in the laboratory, the second, a special typhoid culture and synthetic phenol sent out by the Committee. The 120 results were submitted to a careful analysis and comparison. The following conclusions were drawn:

1. Under all procedures the agreement between the three check determinations was as close as the nature of the test permits *i. e.*, within one dilution or one time interval.

2. In all cases the phenol values used in dividing were in equally good agreement as between the various procedures in the same laboratory, showing that no great part of the variation is attributable to variations in phenol or in organism.

3. Each laboratory showed a distinct "laboratory variation" whereby it tended to be uniformly higher or lower than the average of all five.

4. As between laboratories, the average deviation from the mean was, with one disinfectant (coefficient about 5), 10 per cent. for the H-L method and 18 per cent. for the R-W; with the second disinfectant (coefficient about 15), 6.5 per cent. for the H-L and 14 per cent. for the R-W; or approximately twice as great a discrepancy between the five laboratories when using the R-W method as when using the H-L (three of the laboratories regularly used the R-W method and four of them, the H-L).

5. The H-L method was, in the final average, 5 per cent. higher than the R-W, on the one disinfectant and 11 per cent lower on the other.

In view of the showing of the work of these five laboratories, all skilled in disinfectant testing, it was concluded that some further changes were necessary in the technique in order to

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render it available for general use. Evidence had accumulated in the meantime that the media employed in the standard procedure were too acid for satisfactory results. Reports were received of difficulty of obtaining good growths in the broth and hydrogen ion determinations indicated excessive and variable acidity.

At this point Mr. Wright undertook a special study of this phase of the problem the results of which have already appeared in print.[3] He was able to demonstrate a definite dependence of the observed phenol coefficient upon the degree of acidity of the broth employed and also the advantage, in uniformity of results, of broth approximately neutral in true reaction. He also considered the suitability of certain American brands of peptone.

During 1916 a second extensive comparative test was planned and carried out by the same group of laboratories, the collaborating laboratories representing at this time, however, the Association of Disinfectant Manufacturers. The broth used was unadjusted and practically neutral, and some minor modifications were introduced in the method of preparing the typhoid culture. The results of this test were much more satisfactory. The average deviation from the mean for all H-L tests was 6.75 per cent. and for all R-W tests 4.6 per cent. The work in this case was divided so that three laboratories worked with each test. With the range of phenol dilutions employed the successive dilutions vary by about 10 per cent. which fixes the lower limit of error of single test. Three laboratories making three tests each should report an average deviation of about 3.3 per cent. if all other sources of error are eliminated. It is probable, therefore, that the technique devised is free from sources of gross error and that no further refinement of technique will permit much greater accuracy than that reported. It is also worthy of comment that with the same media the two major methods are of approximately equal accuracy and furthermore that they yield results that are quite concurrent. For the whole series the H-L results are 1.5 per cent. higher than the R-W, a figure well within the range of error between the laboratories and therefore without significance.

The study included also a comparison of Witte's and Armour's

[3] Wright, J. H., *Journal of Bacteriology*, Vol. 2, No. 4, 1917.

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peptones and indicates a uniformly higher result with the former averaging about 7 per cent.

The recommended technique is based upon the results of these investigations.

The most important change that has been recommended is in the media employed. Our investigations in this direction have been referred to. The acidity of the media recommended by Anderson and McClintick is not only too high for satisfactory growth of the test organism, but is also extremely variable, not only among the several laboratories, but from time to time in the same laboratory. By the application of the newer views of acidity, as set forth by Clark and Lubs[4], it has been found that media made without any attempt at adjustment are not only more suitable for the growth of the organism but are far more uniform and reliable.

The hydrogen ion concentration of the culture media is of the utmost importance and it is recommended that each batch of medium be tested for hydrogen ion by the colorimetric method described by Clark and Lubs.

It has been found that the hydrogen ion concentration most conducive to uniform results is approximately $P_H = 6.5$.[5] However, any medium made according to the formula recommended may be used provided the P_H value does not vary more than one-half unit from this figure. Several brands of peptone were studied in detail and of these, two, Witte's and Armour's, were tried in the comparative work done in the five laboratories.

It is recommended that Witte's peptone be used for all important work. The Committee's experience shows, however, that Armour's peptone gives results closely approximating those obtained by Witte's although somewhat lower, so that this product may be used for routine control purpose. It should not, however, be employed unless the hydrogen ion concentration of the finished medium falls between $P_H = 6$ and $P_H = 7$. Care should also be exercised in interpreting the results obtained with this peptone and too much reliance should not be placed upon such results unless the particular lot of peptone in question has been

[4] *Jour. of Bact.*, II, 1917, pp. 1, 109, 191.

[5] The symbol, P_H, stands for the log. of the reciprocal of the hydrogen ion concentration, in terms of normal.

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thoroughly tested and found to be in every respect comparable with Witte's peptone. So far as the work of the Committee has gone, no other brand of peptone may at present be substituted for Witte's. Several manufacturers, however, have recently made changes in their processes of manufacture. In every case the newer products have, with the small number of samples tested, given quite satisfactory results so that it is probable that other products may, upon further investigation, prove available. Some variation has been found in the meat extract, especially in the matter of acidity but there appears to be no satisfactory way of standardizing this product. The Committee wishes to point out the need for further studies upon peptones and meat extract and to invite the co-operation of other bacteriologists in the work.

It has been suggested as a possible solution of the difficulty of variable media that a stock of one or two disinfectants be carried at some central laboratory, such as the Hygienic Laboratory of the U. S. Public Health Service at Washington and that specimens of these be submitted upon request with a full determination of the constants under the approved standard procedure. Such standard specimens would serve as a basis for the standardization of the technique and media of the individual laboratory, including also the strain of organism and the particular sample of phenol used. Such a program would involve among other things consideration of the permanence of the standard disinfectants selected. A still more desirable procedure would be the complete determination of the biological constants of another standard substance, capable of being prepared and kept in pure and permanent form and having a coefficient of from 3 to 5, and a concentration exponent other than 6. With such a second known standard available it would be possible for any laboratory to control its entire technique including all variables in organism or the composition of media. It would then be possible to make such minor changes as the substitution of another brand of peptone or extract in the media with assurance that the results would not be modified. A full investigation of this matter is now under way.

The studies of the Committee have indicated that slightly lower phenol coefficients are obtained with the new media than with the old. A change of this sort, while, in one sense, perfectly fair to

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all manufacturers, would be distinctly troublesome if it necessitated a change of labels and difficult explanations to customers. The slightly increased average time of testing has, therefore, been adopted not only to offset this reduction in coefficient, but also to give proper range to the time factor determination. By reasons of its great relative inaccuracy the 2.5 minutes test has been abandoned, and in order to economize both labor and materials, only those tests are completed which are required in the final computations.

Some studies of the constancy and reproducibility of the platinum loop have shown what has always been more or less obvious that as an instrument of even approximate accuracy, the loop is seriously deficient.

The new loop which is recommended was suggested to us by Dr. Arthur G. Stimson, Assistant Director of the Hygienic Laboratory, Washington, and has been carefully tested as to its reproducibility and its constancy. Comparative tests have been made also with the present standard loop. A strong solution of methylene blue in standard broth was substituted for the bacterial culture, "inoculations" being made into small tubes containing 7 cc. of distilled water. The resulting colors were read against a set of standards. In this way the amount of solution removed by each inoculation was readily determined. Ten loops were prepared and tested, the mean volume taken up by each one being determined by the average of ten "inoculations." The variation among these ten averages is taken as a measure of the reproducibility of the loop, *i. e.*, the agreement between the average performance of various loops. Six standard platinum loops were compared in the same way.

The volumes (average of ten readings each) actually taken up by the ten new loops were, in arbitrary units, 4.90; 4.94; 4.95; 4.98; 4.99; 5.01; 5.06; 5.08; 5.28; average 5.03, mean deviation 0.077 or 1.53 per cent. It is apparent that most of this error is due to one loop, omitting which, the results of nine tests would be, average 5.0, mean deviation 0.05 or 1.0 per cent. For the six standard platinum loops the volumes taken up were (average of ten trials each) in the same arbitrary units, 3.83; 3.89; 4.12; 4.15; 4.26; 4.46; average 4.12, mean deviation 0.17 or 4.10 per cent.

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The mean error of the individual dip as compared with the average of ten dips with the same loop, measures the constancy of the loop. For the one hundred trials made with the ten new loops this mean deviation was found to be 2.52 per cent. and for sixty trials with the six standard loops, 9.28 per cent.

The two kinds of error may be combined to give a general measure of error of each type of loop by counting the mean deviation of all the readings of all the loops of each type from their general average. This procedure gives for the ten new loops, average volume of one hundred trials, 5.03; mean deviation 0.136 or 2.71 per cent., and for the six standard loops, average volume 4.12; mean deviation 0.413 or 10.0 per cent.

The new loop is approximately equal to the present standard loop in volume, the average volume of the ten new loops being 5.03 arbitrary units and the corresponding volume of the standard loop, 4.12.

A modified system of dilutions is recommended which is both simpler and more consistent than the older one. In the selection of a proper range of dilutions attention must be given to the accuracy required and possible. As the coefficient is a ratio the accuracy is also relative, that is, a certain percentage of the final results. An ideal dilution schedule would, therefore, proceed as a geometrical progression, each successive dilution being a constant multiple of the preceding one. The practical difficulties of such a scheme are greater than its advantages would justify so that the expedient has been adopted of dividing the whole range into groups, the mean terms of each group being in geometrical progression, and the members of each group in arithmetical series, that is, advancing by equal increments. This increment is 10 per cent. of the number occupying the position of geometrical mean of each group, and 7 per cent. and 12.5 per cent. respectively, of the end numbers of the group. This arrangement simplifies the making of dilutions since the whole spacing of the system is uniform, each group being similarly related to its basic dilution.

Section B. Standard Procedure.

The following systematic procedure, taken in part from the progress report of the Committee for 1911, is set forth especially

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as an aid to beginners, and to illustrate the fact that certain details are subject to considerable variation without affecting the important features which make for uniformity of results.

Apparatus.

Sub-culture Tubes.—A test tube rack of eight rows of ten holes each may be used for the sub-cultures. If the test be of twenty dilutions, eighty tubes are numbered serially and placed in the rack, which is placed conveniently at the worker's left hand.

Bunsen Burner.—A bunsen burner, with a fan-tail top is led from the left and back of the bench with a little spare tubing.

Loop-rack.—This is made of four pieces of half-inch wood, each 4 inches by 9 inches, joined in a frame so that the top is about 10 inches high. The top is provided with about six grooves for the loops. The latter are placed in their grooves and the rack is placed in front of the worker's right shoulder, close to the front of the bench, and almost at right angles to the front edge, but with a slight slant to the right and rear. The loops point to the left and the fan-tail burner is so adjusted as to properly envelop the loop which is over it. The loops are used in succession and after each one is returned to its place, the burner is moved under it, thus providing at all times for a sterile and cool loop.

Loops.—The loops used for transferring the culture after exposure to the disinfectants are made as follows:

A close cylindrical spiral is made by winding Nichrome wire, No. 23 B. & S.,[6] as tightly as possible about a piece of steel or other hard wire having a diameter of 0.072 inch (No. 13 B. & S. gauge). Wind about five full turns, bend the remainder of the wire sharply at a right angle to the wound portion, and parallel to the axis of the cylinder. Remove from the core and cut off the lower end to leave exactly four complete turns. When completed the successive turns of the spiral must touch one another continuously. See Fig. 1.

Seeding Tubes.—The character of the seeding tubes to be used depends entirely upon local conditions. In places in which there is any doubt as to air contamination cotton-plugged tubes are much to be preferred. However under conditions such as exist in most laboratories the open seeding tubes, recommended in the

[6] Manufactured by Driver Harris & Co., Harrison, N. J.

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present standard methods, are most convenient and quite satisfactory.

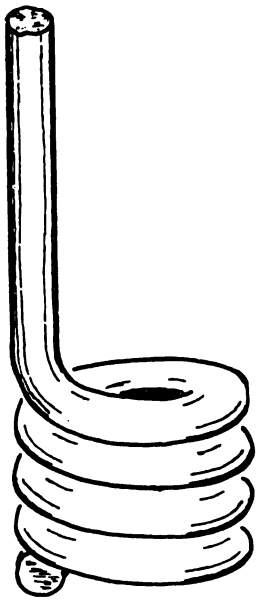

FIG. 1.—NEW STANDARD LOOP.
Four turns of Nichrome Wire, No. 23, B. & S., about a core, 0.072 inch in diameter (No. 13, B. & S.)

Seeding Tube Holder.—Cut down an oblong wire test-tube basket to about 2½ inches in depth, and to the top fit a piece of half-inch wood, through which three rows of seven holes each have been bored, the holes being of proper size to accommodate the tubes loosely. An ordinary tripod is used to support this rack in the water bath. The legs of the tripod are cut so that the tops of the seeding tubes are a little above the surface of the water.

Inoculator.—The inoculations of the diluted disinfectant with the culture are made with an apparatus described by Rosenau.[7] A capillary pipette, graduated in tenths cc. is fitted with a rubber bulb, and clamped to a ring-stand. The bulb is actutated by a second spring clamp the jaws of which engage it. This apparatus is placed at the right of the worker, so that he can push the loop

[7] *Hyg. Lab. Bull.*, 21, p. 60.

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rack away from him and draw the inoculator toward him and when through inoculating, reverse the action.

Water Bath.—The water bath consists of a wooden box about 18 inches square and deep, containing a three or four gallon pail, packed around with sawdust which is lightly oiled so as not to become dusty. The bath is raised from the floor about six inches by cleats and castors, and when not in use is rolled under the bench. During the test it is on the floor at the right of the worker.

Time-piece.—A watch or small clock of fair accuracy, provided with a second hand, is so mounted as to be conveniently and comfortably read by the worker from his place at the bench.

Culture Media.

The culture media are prepared as follows:

Broth.—10 grams of peptone (Witte's); 3 grams of extract of meat (Liebig's); 5 grams of sodium chloride, C.P.; Distilled water, 1,000 cc.

Boil for 15 minutes, make up to weight, filter, tube, sterilize at 10 pounds pressure for 20 minutes. No adjustment of the acidity whatever should be attempted. Determine and record the P_H value. This should be between 6 and 7.

Agar.—To 1,000 cc. of the standard broth add 15 gms. of best grade agar, boil 30 minutes, make up to weight, filter, and sterilize at 10 pounds for 20 minutes. Do not use egg albumen to clarify.

Organism.

For the standard test organism in determining the coefficient against the typhoid organism a 24-hour old broth culture of B. typhosus (Hopkins) is used. Before beginning a test the culture is carried over in broth at 37° every 24 hours for at least five successive days, and the last culture well shaken, and filtered through sterile filter paper.

For carrying over the culture one standard loopful is used. It is important that the transfers be made as nearly as possible exactly on the 24-hour interval, although a variation of not more than 2 hours is allowable.

The stock culture of B. typhosus (Hopkins) is kept on agar

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slants. These cultures are incubated at 37° C. for 24 hours and then placed in the refrigerator until ready for use. In no case, however, should they be kept more than one month.

Phenol.

While pure phenol crystals are undoubtedly the best standard which we have at present, they are far from being entirely satisfactory. Commercial phenol crystals are often contaminated with cresols and other phenol homologues. It is important that nothing but the highest grade of pure white synthetic phenol crystals be used,[8] of a solidifying point not less than 40° C. as determined by the method of Weiss and Downs.[9]

Phenol crystals themselves, as well as solutions change in germicidal strength upon standing, particularly when exposed to direct sunlight and to high temperature. Phenol changes more readily when melted, or in the presence of moisture, than when in the crystalline form. It is important, therefore, that the crystals of phenol be kept in a tightly stoppered bottle, in a cool, dry place and exposed to the light and moisture as little as possible. Phenol which has been exposed to the air and allowed to absorb enough water to alter its melting point or which has become at all red should be discarded for the purposes of this test. The 5 per cent. stock solution is prepared as follows:

Melt the phenol in the original container and pour out approximately 50 grams into a closed weighing bottle; weigh and dissolve in the proper amount of water to give a 5 per cent. solution. Do not attempt any further standardization. This stock solution is kept in the refrigerator in amber colored bottles of not more than 500 cc. capacity, and for a period not longer than three months.

Dilutions.

Distilled water.—Sterile distilled water is recommended for all dilutions. Attention is directed to the danger of metallic copper in distilled water prepared with the common type of laboratory still in which the condensing surface is of tin-plated copper or brass. If the tin-plate is worn away, sufficient copper may be dissolved to materially influence the coefficient.

[8] The Barrett Manufacturing Company can furnish such a product.

[9] *Jour. of Industrial Chemistry*, Vol. 9, No. 6, p. 569.

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Five Per Cent. Stock Dilution.—Accurately graduated capacity pipettes are to be used in preparing the stock dilution of disinfectant. Five cc. of disinfectant are measured into a flask containing 95 cc. of sterile, distilled water, the interior of the pipette being rinsed several times with the contents of the flask. From this solution or emulsion and from the stock 5 per cent. phenol solution the required dilutions are prepared.

Initial Dilution from Five Per Cent. Dilution.—Take 50 cc. of the 5 per cent. stock dilution, place in a 100 cc. graduated flask and make up to the mark with sterile distilled water. Mix by pouring.

This gives a dilution of 1 : 40. With 50 cc. of this dilution repeat the process to obtain a dilution of 1 : 80 and so on by successive dilutions until the following initial dilutions, or such of these as are necessary for the test, are prepared:

1 : 20	1 : 160
1 : 40	1 : 320
1 : 80	1 : 640

Final Dilutions from Initial Dilutions.—With sterile delivery pipettes measure the quantities of initial dilutions and sterile distilled water, required, in accordance with the following table, to obtain the desired final dilutions.

	Initial dilution					
	1:20	1:40	1:80	1:160	1:320	1:640
Initial dilution + water (cc.)	Final dilution					
4 + 4	1:40	1:80	1:160	1:320	1:640	1:1280
4 + 5	1:45	1:90	1:180	1:360	1:720	1:1440
4 + 6	1:50	1:100	1:200	1:400	1:800	1:1600
4 + 7	1:55	1:110	1:220	1:440	1:880	1:1760
4 + 8	1:60	1:120	1:240	1:480	1:960	1:1920
4 + 9	1:65	1:130	1:260	1:520	1:1040	1:2080
4 + 10.....	1:70	1:140	1:280	1:560	1:1120	1:2240

Temperature.

The standard temperature at which the organism is exposed to the action of the disinfectant is 20° C. but a variation of not more than 0.5° on either side of this figure is allowable. This temperature should be maintained by the use of a water bath, the design of which may be left to the individual operator. It is

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important, however, that the bath be so arranged that the water will rise to a height greater than that of the dilution of disinfectant contained in the seeding tubes. The cultures and dilutions of disinfectant should be brought to a temperature of 20° C. before starting a test. In very warm weather it will be found that there is a material increase in the temperature of the water bath during the 20 minute period. If, however, the bath is brought at the start to a temperature of 19.5° it will not generally exceed 20.5° during the test. For the determination of the temperature coefficient a temperature of 30° is also employed.

All sub-cultures are incubated at 37° for 48 hours. The temperature of the incubator should be maintained between 36° and 38°.

Technique.

The various dilutions are prepared as already described.

In the test of a new preparation the coefficient of which is unknown it will be necessary to make a set of range-finding tests. For this purpose use the series 1 : 40, 1 : 80, etc., at the head of the columns in the Table of Final Dilutions and select for the actual test with phenol a series of final dilutions ranging from the highest dilution which killed in 5 minutes, to the lowest dilution which failed to kill in 20 minutes. If some approximate idea of the coefficient is available, or if the preliminary test indicates a too extensive range of dilutions for the final test, a closer range may be obtained by restricting the test to fewer columns and using the middle row of dilutions together with the top row.

The seeding tubes having been properly sterilized are brought to the bench and placed in the seeding tube rack to the number required. Five cc. of each of the dilutions of phenol and of the disinfectant to be tested are placed in order in these seeding tubes, which are appropriately numbered, a separate 5 cc. delivery pipette being used for each dilution. The tube containing the filtered culture is next placed in one of the holes of the seeding tube holder which is then placed in the water bath and allowed to stand there for a sufficient time to bring the contents to temperature. The inoculator is then filled with culture and, at the beginning of an even five-minute period, the first seeding tube is inoculated with 0.1 cc. of culture, and the succeeding tubes are then inoculated at appropriate intervals.

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If the manipulator is sufficiently skilled to make inoculations and transfers at 15-second intervals, as at present recommended in the standard procedure, the total number of dilutions including the phenol dilutions, that can be carried through a test simultaneously is 20. Five of these are necessary for the phenol, 1 : 80 to 1 : 120 inclusive, leaving a maximum of 15 for the disinfectant. This will permit the employment of two of the columns of the table of final dilutions if necessary. In practice, however, it will seldom be found necessary to extend the range over more than one complete column or eight dilutions which with five phenol dilutions, gives thirteen in all. This will permit the making of inoculations and transfers at 20-second intervals, with one minute leeway at the end of each round, a safer and more comfortable schedule. For the beginner, 30-second intervals are recommended, which permit the carrying of ten dilutions simultaneously. Whatever the interval decided upon, it is quite desirable that a plan of the test showing the dilutions to be used, intervals between inoculations, and times of making sub-cultures be carefully laid out on paper so that there shall be no confusion in these matters during the actual test. The following will serve to illustrate the value of such a paper plan.

PLAN FOR TEN DILUTIONS AT THIRTY SECOND INTERVALS.

	Seeding tube No.	Dilution	Inoculate		5-min. test		10-min. test		15-min. test		20-min. test	
			Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.
Phenol.	1	1 : 80	00	00	5	00	10	00	15	00	20	00
	2	1 : 90	00	30	5	30	10	30	15	30	20	30
	3	1 : 100	1	00	6	00	11	00	16	00	21	00
	4	1 : 110	1	30	6	30	11	30	16	30	21	30
	5	1 : 120	2	00	7	00	12	00	17	00	22	00
Test...	6	1 : 360	2	30	7	30	12	30	17	30	22	30
	7	1 : 400	3	00	8	00	13	00	18	00	23	00
	8	1 : 440	3	30	8	30	13	30	18	30	23	30
	9	1 : 480	4	00	9	00	14	00	19	00	24	00
	10	1 : 520	4	30	9	30	14	30	19	30	24	30

A set of these plans, covering the more common range of working conditions, might well be prepared in standard form for ready reference.

When the tubes have all been inoculated, the inoculator is pushed away diagonally and the loop-holder is drawn up to the edge of the bench and just before the expiration of the time

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interval, sub-culture tube No. 1 is taken in the hand, the plug withdrawn, and a loop dipped perpendicularly into the first seeding tube. At the expiration of the time interval, the loop is withdrawn, and the transfer consummated. The loop is returned to its groove in the loop-holder, the burner moved in place under it and the sub-culture tube given a rapid whirling movement to mix its contents and replaced. Another tube and another loop are then taken in hand for the next transfer.

At the completion of the test, the sub-culture tubes are placed in the incubator, and 48 hours later they are removed, read and recorded.

The A. P. H. A. Standard Phenol Coefficient,

The concentrations of the highest dilutions of the disinfectant which gave negative results in 5, 10, 15, and 20 minutes respectively, are divided by the corresponding concentrations of phenol to obtain a series of four coefficients. The arithmetical mean of the four is taken as the "Mean Phenol Coefficient against Typhoid, 20° C., 5-20 minutes, A. P. H. A." It is recommended that a final report should be based upon the results of not less than three separate tests. This coefficient will be known for brevity as the "A. P. H. A. Standard Phenol Coefficient," but for any other organism, temperature or time ranges that may be employed the word "Standard" will be omitted and the full expression given. The determination of these special coefficients for special uses is recommended.

Units Employed.—It should be observed that the customary procedure of weighing the phenol and measuring the disinfectant by volume, gives a coefficient which is actually expressed in two sets of units. Strictly interpreted, this coefficient gives the relation (under the conditions of the test) between one liter of the disinfectant and one kilo of phenol, or between a gallon of disinfectant and 8.34 pounds of phenol. Comparison upon a weight basis may be obtained by dividing the coefficient by the specific gravity of the disinfectant, or by making the initial 5 per cent. stock solution by weight. This latter procedure is necessary in testing a solid substance and if in any case it is resorted to, the results should be expressed as "A. P. H. A. Standard Phenol Coefficient (by weight)." This procedure also permits the study

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of the disinfectant powers of water soluble gases and the reporting of the results by weight.

Stability of Emulsions.—The great majority of commercial disinfectants are prepared by emulsifying coal tar distillates, and it is important that these products should form uniform and stable emulsions when diluted with water. It occasionally happens that poorly manufactured products of this type form perfectly stable emulsions in the range of dilutions used in determining the coefficient, while in a more concentrated solution the greater part of the germicidal power is lost, owing to the breaking down of the emulsion and separation of the active constituents. It is recommended therefore that, when testing this type of preparation, 100 cc. of a dilution of the same strength as that to be used in actual disinfection be allowed to stand in a tall cylinder at room temperature, for 24 hours. There should be no appreciable separation of oily material at either top or bottom.

Occasionally products are found which do not form stable emulsions in the range of dilutions used in determining the coefficient. If the separation is rapid the results of the test may be very irregular, so that it is practically impossible to determine the coefficient. Such a possibility should always be considered in looking for the explanation of irregular results.

The phenol coefficient determined under carefully standardized conditions is believed to be a reliable means for ascertainig the relative values of that class of disinfectants prepared by emulsifying coal tar distillates. It is also believed to be suitable for the routine control of manufacturing processes and should be employed for this purpose by all manufacturers. With disinfectants of varying chemical or physical nature the simple coefficient may be misleading. This phase of the problem is discussed in detail in Section C. and some additional determinations are recommended, which should prove of value in showing how disinfectants of different types vary under varying conditions of practice.

Section C. Theoretical Considerations.

Principles of Disinfectant Testing.

In order to make the results of the test somewhat more directly

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applicable to different types of disinfectants under varying conditions of practice, and in order further to emphasize the limitations that restrict the use of the phenol coefficient and to remove these limitations as far as possible, the scope of the test has been somewhat extended and certain new biological constants have been made available thereby. The significance of these limitations and of the new data that will be made available by the proposed changes will therefore be discussed in some detail.[10]

The germicidal power of any disinfectant, as it is usually measured in terms of time to sterilize, is affected by such factors as the specific resistance of the organism, the medium on which the disinfection is carried out, the number of organisms present in unit volume, the concentration of the disinfectant and the temperature at which the test is made. It is apparent, therefore, that a statement of the properties of a disinfectant must, if it is to be of practical service, describe the effect of each of these variables upon the germicidal power of efficiency. A realization of the difficulty of such a complete study and record of the large number of existing disinfectants and of the utter inadequacy of existing data upon even the simpler disinfectants and the more common pathogenic organisms, led Rideal and Walker (2) to the conception of a coefficient which would measure not the absolute effect of the disinfectant, but its relative effect as compared with some standard substance.

Phenol was chosen for the standard and the relation between the dilution of the disinfectant in question and that of phenol capable of exerting an equal germicidal effect was called the carbolic acid coefficient.

It is evident that if phenol and the disinfectant under examination be equally affected by variations in the numerous controlling factors outlined above, then their relative germicidal values, and consequently the coefficient will remain unaffected or constant. This would be the case, for example, if an increase in temperature resulted in each case in an equal proportionate increase in the rate of killing, if doubling the concentration increased the rate to the same relative extent in each case, and if the resistances of various strains of organisms, the varying composition of the

[10] For more complete discussion see Phelps, *Jour. Inf. Dis.*, 8, 1911, 27, and Phelps, *Amer. Jour. Pub. Health*, 3, 1913, 53.

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medium in which the organism is grown or the test made, and the numerous other variable factors, produced the same relative effect upon the germicidal efficiency of the two disinfectants. If all these suppositions were true, then there would be a single phenol coefficient for each disinfectant and the conditions under which the test is made would be immaterial. The early history of the test indicates that this was believed to be the case, and the phenol coefficient is even now almost universally accepted as a measure of the strength of any type of disinfectant against any pathogenic organism and under all conditions of practical application. This is particularly shown in the use of the coefficient in specifications, in labeling and advertisements, and in the determination of relative price values.

On the other hand, those familiar with the details of the test are fully aware that there are many possible "phenol coefficients" depending upon the conditions of testing, that particular coefficient which is obtained by testing under the standard conditions, being but one of this number.

It measures, therefore, the value of the disinfectant in question under those particular standard conditions and relative to phenol, and other conditions would furnish other measures of relative value.

Fortunately for the cause of disinfectant testing it seems to be the case that this variation in phenol coefficient is due to the difference in chemical and physical natures of the two disinfectants and that the less these differences between any two disinfectants the more nearly constant will be the relation of their respective efficiencies under variable conditions of testing. Chick[11] had shown for example that the phenol coefficient of mercuric chloride at 2.5 minutes is 13.6 and 30 minutes, 550, while on the other hand evidence is accumulating which tends to show that in that group of commercial products made by emulsifying coal tar distillates, the variability is reduced to a minimum.

These products, being unlike a phenol solution, have variable coefficients with varying time and concentration, but among themselves, the variation is similar so that their phenol coefficients determined under well standardized procedure, giving their true

[11] *Jour. of Hyg.*, 1908, 92.

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values relative to phenol under one set of conditions, serve to grade them among themselves under all other physical conditions. In this case the phenol coefficients of emulsified coal tar disinfectants do measure the relative value of those products that are somewhat similar in chemical or physical properties, and the greater the dissimilarity among such products or between them and other types of disinfectants, the less reliable is the coefficient as a measure of relative valuation.

It is apparent, therefore, that if disinfectants of different types are to be rated and compared by any single coefficient, the effects upon the coefficient of the more important variables, at least, must be taken into consideration. Just as the complete statement of the electrical conductivity of a metal includes its conductivity at one stated temperature together with the thermal coefficient or effect of varying temperature upon the conductivity, so a complete statement of the phenol coefficient must include the coefficient under fixed conditions and a measure of the effect of varying conditions.

In so far as this effect of variable conditions is in itself constant, as determined by the constancy of certain additional factors to be described, just so far is it permissible to compare the disinfectants under consideration upon the basis of their phenol coefficients. In other cases, and particularly among disinfectants of varying types, a full comparison of properties must involve a further statement of the effect of variable conditions upon the efficiency of the disinfectants tested.

In view of the somewhat general use of the phenol coefficient as a standard basis of reference it would seem desirable to continue this standardized specific measure as a point of departure, with a more complete statement of its limitations than has hitherto been made. It is also highly desirable to extend the practical usefulness of this measure by removing from it certain of the experimental restrictions that have hitherto been imposed, thereby broadening its scope and significance.

The most important restriction is the organism used in the test. The trend of the time is strongly towards specific and away from general disinfectants. No further recommendations are made in this connection, however, than to point out the possibility that

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the coefficient as determined with one organism may have no significance in connection with another and the urgent desirability of extensive studies of various types of disinfectant upon various pathogenic organism. In such a study the general procedure recommended for the typhoid organism should be followed, with such modification as to media and other details as may be found necessary.

The second important variable to be considered is that of concentration. The efficiency of a disinfectant, measured in terms of rate of killing, or time to sterilize a given volume, containing a given initial number, is not proportional to its concentration, but to some power of that concentration depending upon the nature of the disinfectant in question. With phenol the rate of killing varies approximately as the sixth power of the concentration. If, with the disinfectant under study, it varies as the fourth power, and if the concentrations necessary to kill in 2.5 minutes are found to be 1 : 80 and 1 : 400 respectively, then those necessary to kill in 15 minutes (one-sixth the rate of killing) would be respectively, 1 : 108 and 1 : 626, giving coefficients for the two time periods of 5.0 and 5.8. Under the procedure adopted by Rideal & Walker a single time period was adopted. The Lancet method gave some recognition to this variable feature by averaging the two coefficients obtained at 2.5 and 30 minutes and the Hygienic Laboratory method takes similarly the 2.5 and 15 minutes results. In view of the significance of this coefficient variation with the time of exposure it is believed that it should be measured and reported rather than concealed in an average.

To this end it is recommended that separate coefficients be determined at 5, 10, 15 and 20 minutes; the mean of these values being taken as the "mean A. P. H. A., phenol coefficient 20° C., 5-20 minutes," or, for brevity, the "A. P. H. A. standard phenol coefficient;" and that the ratios between the 5 and 10 minutes, and the 10 and 20 minutes values be computed, averaged and reported as the "time ratio."

The time ratio as thus determined bears the following relation to the concentration exponent, R being the ratio of the coefficient determined for any time of exposure, to the coefficient for twice that time of exposure, and n, the concentration exponent, which

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shows by what power of its concentration the efficiency of a disinfectant varies:

$$\log R = 0.05 - \frac{0.3}{n}.$$

For more ready interpretation of the significance of the time ratio, the following table shows for each value of the ratio R, the corresponding value of n, and the relative increase in the germicidal power of the disinfectant corresponding to a doubling of its concentration. These last named values are given by the expression 2^n, the germicidal value varying as the *nth* power of the concentration.

RELATION BETWEEN THE "TIME RATIO," R, THE CONCENTRATION EXPONENT n, AND THE INCREASE IN GERMICIDAL POWER OF A DISINFECTANT RESULTING FROM A DOUBLING OF ITS CONCENTRATION IN THE MIXTURE.

Time ratio R	Concentration exponent n	Relative germicidal power of a mixture of double concentration, 2^n
0.1	0.29	1.2
0.2	0.40	1.3
0.3	0.52	1.4
0.4	0.67	1.6
0.5	0.85	1.8
0.55	0.97	2.0
0.6	1.10	2.2
0.65	1.27	2.4
0.7	1.46	2.8
0.75	1.72	3.3
0.8	2.04	4.1
0.85	2.49	5.6
0.9	3.13	8.8
0.92	3.48	11.1
0.94	3.90	15.0
0.96	4.43	22.0
0.98	5.10	34.0
1.00	6.00	64.0
1.01	6.57	95.0
1.02	7.25	152.0
1.03	8.07	267.0
1.04	9.09	544.0

The significance of the concentration exponent has to do with the use of a disinfectant in various concentrations. A disinfectant with a high exponent, like phenol, will have its germicidal power increased at a rapid rate with increasing concentration and de-

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creased equally rapidly with increasing dilution. Such a disinfectant will be said to possess low antiseptic powers for on dilution the germicidal power is rapidly "diluted out." One with a low exponent will increase more slowly in germicidal power with increasing concentration and decrease more slowly with increasing dilution. It would be classed as a good antiseptic. Phenol with an exponent of six is of the first type and mercuric chloride, exponent one, of the second.

A third important variable, carefully controlled in the test of a disinfectant, is the temperature. In order to obtain consistent phenol coefficients it has been found necessary to adopt a standard temperature of testing. The recommended procedure specifies a temperature of 20° C. It is obvious, however, that practical working conditions will not always conform to this standard and, the phenol coefficient being actually dependent upon the temperature selected for the test, cannot measure the true relative value of the disinfectant at other temperatures. It is known that many disinfecting reactions, like chemical reactions in general, have a definite temperature coefficient which measures the proportionate increase in the rate of the reaction (or decrease in time of completion) for a stated increase in temperature. It is important to note the form of this relation. The increase in rate is proportionate, as the temperature increases by equal increments. The physico-chemical law is thus expressed:—

As the temperature increases in arithmetical progression the velocity of reaction increases in geometrical progression. Thus, if a rise of 10° doubles the rate, a further rise of 10° will double it again so that an increase of 20° will quadruple it. The temperature coefficient, usually expressed for a 10° interval, gives the ratio of the rate of reaction at the higher temperature to that at the lower. In the case of disinfection the respective times to complete the reaction may be taken inversely as the rates so that the temperature coefficient for a 10° interval will be the ratio of the longer to the shorter one.

Little exact knowledge is available as to the temperature coefficients of disinfectants but their importance in practical disinfection is such as to justify careful study and record in the case of any disinfectant worthy of serious consideration. By the simple expedient of determining the relative times of sterilization

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at two different temperatures under otherwise comparable conditions, the temperature coefficient is readily determined. As between two disinfectants, the one with the higher temperature coefficient will show the greater rate of increase in efficiency at higher tempeature, and of decrease at lower. A comparison of the temperature coefficients will therefore disclose those disinfecants particularly suited for use at low temperatures or at unusually high temperatures. For use at temperatures above the standard employed in testing, a high temperature coefficient is desirable and vice versa.

It might appear that the examination of a disinfectant is becoming an increasingly serious matter, but it is believed that any simpler formula than that outlined not only fails to describe the disinfectant, but, if applied to preparations of different types may be actually misleading and capable of doing harm. A disinfectant which has been studied and described in accordance with the principles outlined above, may be said to have had its bacteriological constants fairly well detemined. To this end the following determinations are recommended in addition to the standard phenol coefficient:

(*a*) The determination of the coefficient against disease producing types of bacteria other than B. Typhosus particularly the ones against which the disinfectant is to be used.

(*b*) The temperature coefficient; and

(*c*) The concentration exponent or "time ratio."

From a theoretical point of view the phenol coefficient is eminently unsuited as a starting point for the determination of these new constants. In view, however, of its general adoption and legal recognition and of the much greater difficulties of technique involved in a more accurate and fundamental determination of the reaction constants of a disinfectant, the recommendations for the determination of the concentration exponent and temperature coefficient are based upon the recognized procedure.

Determination of the Temperature Coefficient.

That concentration of the disinfectant which killed in 20 minutes and was, therefore, employed in computing the phenol coefficient at the 20-minute period is again taken for the temperature coefficient test. Four identical mixtures of disinfectant and

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culture are prepared exactly as in the previous case except that two of these are contained in a special temperature bath at 30° C. The successive mixtures are made at 30-second intervals, the two 20° tubes being prepared first. At one minute intervals from the time of mixture a sub-culture is made from each of the two 30° tubes, this procedure being continued up to the eighth set and then continued upon the 20° tubes from the tenth to the twenty-second minute. Incubate, read and record the results as previously. Take the average time to kill at 20° C. from two tests at that temperature and similarly for 30°.

The Temperature Coefficient for Ten Degrees.—Divide the least time required for sterilization at 20° (average of two tests), by the similar time at 30°, other conditions being the same. The quotient is the temperature coefficient for 10°. The coefficient for 5° is the square root of the 10° value, and that for one degree the tenth root. The 10° coefficient is usually employed in chemical literature and may be computed from the value for any other temperature range such as x degrees by taking the $\frac{10}{x}$ power of that value.

The Time Ratio and Concentration Exponent.—These are related constants and only one of them need be reported. The time ratio is the ratio between the coefficient determined at any time period and the similar coefficient determined at twice that time period. Under the standard procedure divide the 5-minute by the 10-minute coefficient and the 10-minute by the 20-minute coefficient. Average these two quotients and report at the time ratio; compute the concentration exponent by formula or read it from the Table, page 497.

A complete study of a disinfectant must also include its physical and chemical behavior in the medium in which it is to be employed, as for example, its diffusibility or powers of penetration, and especially its chemical permanence. These are matters demanding careful investigation but as they vary from case to case it would be hopeless to attempt to include them in a general specification of the disinfectant. There is urgently needed, however, a comprehensive study of these practical phases of disinfection. Beyond such obvious chemical facts as the failure of acid

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as a disinfectant in an alkaline medium, of an oxidizing disinfectant in a reducing medium, or of a heavy metal disinfectant in a precipitating medium, but little is known of the chemical behavior of disinfectants in the media commonly encountered. The surprising effects of common salt upon a solution of phenol and of ammonia upon hypochlorite are but indications of the importance of this whole subject.

Constants to be Reported.

It is believed that a single phenol coefficient is a sufficient basis for a preliminary classification of disinfectants and for the exclusion of worthless trade preparations and that furthermore it forms a reliable basis for the relative valuation of disinfectants of similar chemical and physical nature, particularly the emulsified coal tar preparations. To this end a reputable trade product should always be accompanied by a statement of its coefficient preferably in terms of the "A. P. H. A. standard Phenol Coefficient." This single value, however, gives inadequate indication of the usefulness of all types of disinfectants under other than laboratory test conditions and should be regarded more as a presumption than as direct evidence of quality. The time factor or the concentration exponent furnishes much more detailed information of the action of the disinfectant upon typhoid organisms at various concentrations and ought always to be determined. The temperature coefficient ought also to be carefully studied by an investigator proposing to undertake disinfection under temperature conditions unlike those of the test.

These three tests against typhoid should be considered in preparing specifications, and manufacturers and dealers should be prepared to specify values for the guidance of health authorities and others.

Finally disinfectants intended for special purposes should be standardized against the particular organism in question and the report should so indicate. As far as practicable also the test should be under standardized conditions simulating those of practice and the report should so indicate. In particular attention must be given to the general chemical nature and reaction of the disinfectant and to incompatible mixtures and interfering chemical reactions.

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There remains to be determined and made available a large amount of definite and practical information concerning the action of disinfectants of various types upon various important pathogenic organisms so that the general relationships existing between the relative resistances to each general type of disinfectant shall be available. To this end the most thorough-going and complete tests and application must be made by public health research laboratories. Such studies are necessary for the construction and understanding of a proper theory of disinfection.

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ABSTRACTS.

Theory of the Cause of Salt Stains on Leather. W. MOELLER. *Collegium*, 1917, 7-14, 55-59, 105-124, and 153-161; *Z. Angew. Chem.*, 1918, 31; *J. S. C. I.*, 1918, 342A. A "physiological" tanning process in either the living or dead organism is regarded as the cause of salt stains. Various substances may act as tanning agents, *e. g.*, iron or sulphur, melanines or sulphur, and iron bacteria. The stains are due to very small quantities of the active substances. The most important preventative is the use of some alkali as a preserving or curing agent. The tanning cannot take place in the presence of alkali.

Fermentation of Vegetable Tannin-Colloids. W. MOELLER, *Collegium*, 1917, 49-55; *Z. Angew. Chem.*, 1918, 31; *J. S. C. I.*, 1918, 341A. Tannins like polyhydric phenols are converted by certain enzymes (polyphenol oxidases) into humic acids, a change involving simultaneous oxidation and condensation with considerable loss of tanning power. As such fermentation may occur at any time during the storing or use of extracts, tanners should ascertain to what extent formation of humous matter has taken place and should reject extracts in which the fermentation has been considerable. Phenol, thymol, toluol and other substances, inhibit or entirely prevent the process.

Determination of Free Sulphuric Acid in Leather. H. STRUNK and O. MATTHES. *Z. Angew. Chem.*, 1918, 31, 61-63; *J. S. C. I.*, 1918, 383A. Thirty cc. of magnesium nitrate solution (containing about 0.2 gram MgO) is heated in a round-bottomed flask until an almost dry residue remains; 5 grams of the leather and a few cc. of 30 per cent. nitric acid are added and the mixture is heated on a water-bath until reaction ceases. Fifty cc.

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of concentrated nitric acid is then added, the mixture boiled on a sand-bath for 2 hours, heated over a flame until all the nitric acid has been expelled, cooled, again heated with concentrated nitric acid, and evaporated. The dry material is strongly heated to decompose nitrates and expel nitrous fumes from the flask, and the almost white residue is dissolved in 30 cc. of *N/2* hydrochloric acid, filtered if necessary, and titrated with *N/10* sodium hydroxide solution, using phenolphthalein as indicator. Another portion of 30 cc. of the magnesium nitrate solution is evaporated, heated to decompose the nitrate, the residue dissolved in *N/2* hydrochloric acid, and titrated with sodium hydroxide solution. Less sodium hydroxide solution will be required in this titration than in the case of the residue from the mixture containing the leather if free sulphuric acid is present; the sulphuric acid combines with a portion of the magnesium oxide, and the difference in the two titrations is a measure of the quantity of free acid present.

Alumina and Silica Content of Leather Ashes. M. GONNERMANN. *Collegium*, 1918, 78; *J. S. L. T. C.*, 1918, 188. Alumina and silica are normal constituents of both human and animal organs. In various fat and vegetable tanned leathers the silica was found to constitute 21-41.5 per cent. of the ash whilst the alumina even reached 60 per cent. in one case. In chrome leathers, the ash was repeatedly evaporated to dryness with concentrated hydrochloric acid, to render the silica insoluble and the alumina soluble. Having removed the alumina the residue was fused with ammonium fluoride and thus a residue of chromic oxide was obtained. The silica content is connected with the resistance of the products. Kobert thinks that by suspending skins in water containing silicic acid the resistance of the leather produced from them will be greatly increased.

The Aldehyde Tannage I. W. MOELLER. *Collegium*, 1918, 25-40; *J. S. L. T. C.*, 1918, 188. Tanning depends somehow on the tanning material being neutral or acid, and not on its containing a "tannophore" group. The colloidal condition seems to be essential also. Fahrion's objections (*Collegium*, 1917, 320) to the author's theory are first discussed. He objects to the "peptiser" being said to be "adsorbed" and thinks there is a solid solution. Many authorities are quoted to show that there is no definite cenception of the difference between the two phenomena. Lauffmann describes the author's view; "The hide substance adsorbs the 'peptiser' (Peptisator) from the sol, and the gel which is separated out, surrounds the hide fibers in the form of micro-crystals as a thin previous layer whilst the 'peptiser' diffuses through the membrane thus formed, and forms a solid solution with it."

With regard to the aldehyde tannage, Fahrion states that by hydrolysis of hide substance, gelatine peptones are formed, which can be precipitated by tannin, and free amino acids, which give a precipitate with formaldehyde. Free amino acids however form soluble compounds with HCHO, and gelatine only gives a stiff, transparent insoluble jelly with HCHO.

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If Fahrion's assertions were correct, they would afford valuable evidence for the chemical theory of this tannage and this serious error has no doubt been of great assistance in building up Fahrion's chemical theory. There is a very distinct chemical action between HCHO and free amino acids but not a precipitation as Fahrion incorrectly asserts. This fact is of very great importance in explaining this tanning process, since one has to take into account the presence of free amino acids in the interstices of the hide after it has been suitably bated for the process. The fact that the products with which HCHO reacts chemically are liquid and soluble, is in the author's opinion a direct proof that the products due to stiffening with HCHO are not chemical compounds.

Most histologists agree with Schiff's chemical theory that 1 molecule HCHO reacts with 2 atoms of hydrogen in a primary amine residue. This has not been proved and most facts point to the contrary. Fahrion cites insolubility as a proof of the chemical combination of HCHO with undecomposed protein compounds but most of them form soluble compounds with HCHO. It is purely arbitrary to suppose that only primary amine groups in the protein molecule react with HCHO. The amount of HCHO is too small compared to the collagen to be able to unite with it in accordance with the laws of stoichiometry, but it may just be sufficient to react with the hydrolytic dissociation products present in the hide or on the fibers as a result of bating.

Fahrion claims that HCHO effects a chemical change on the hide fiber because hide powder takes up less acid after a treatment with HCHO. The author attributes this to the change in physical condition from hide powder to leather powder. The stoichiometric relationships which would enter into any possible chemical reaction between collagen and HCHO, cannot be expressed in a simple manner as Fahrion has done, for present research shows the very complex matter of the protein molecule, possessing several free amino groups and also free guanidine groups. A simple formulation of the tanning process on a chemical basis is inconceivable.

The author agrees to a large extent with Thuau who points out that HCHO easily polymerises, especially in presence of alkali carbonates, and thinks that the conversion of crystalloid HCHO polymers into colloidal polymers is facilitated by the hide substance itself. The author proposes to show by experiment that an aldol condensation does take place and provides a theoretical basis for this tannage. Comparison is made with Kann's work on wool (*Farber Zeitung*, 1914, 73), who concludes there are no free amino or keto groups in the wool molecule.

Two components must always be present in the tanning materials, the "peptiser" and the peptised substance. Neither of these can tan alone, nor can any hydrosol unless a peptiser is present. The peptiser may be absorbed by the hide substance, but it alone cannot tan, and this explains the contradictions so often met with by investigators on the tanning problem, who think they have made a great discovery if they find a compound which is taken up by hide powder. Phenol is thus adsorbed

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but it does not tan, in fact phenol is one of the best solvents of gelatine. It is a characteristic of all "peptisers" that they are capable under certain conditions of causing the hide substance to pass into solution, in such a manner that they are distributed through the hide in the form of a solid solution, so that by further prolonged action they can pass into liquid solution.

This property has long been known with the tannin "peptiser" and its solvent action on the hide substance comes into play if a sufficiently concentrated tannin solution is used and if at the same time the small amounts of peptised substances in the tannin are converted into a true solution by the addition of an organic acid or precipitated by the addition of small amounts of inorganic acids; the condition of peptisation is destroyed, which is present to a small extent even in the purest tannin. All peptisers are capable of forming solid solutions with the hide substance and also of forming true solutions in an aqueous medium without showing the slightest trace of leather forming qualities.

Aldehyde Tannage I. (*contd.*). W. MOELLER. *Collegium*, 1918, 61-71; *J. S. L. T. C.*, 1918-190. The fundamental principle underlying the aldehyde tannage is not the aldehyde group itself but the colloidal character. Aldehydes which do not form colloidal polymers or cannot be peptised have no tanning effect. Formaldehyde can form paraformaldehyde and several polyoxymethylenes. Experiments done by the author showed that formaldehyde alone had little tanning effect, but in conjunction with alkali this effect was much increased. It was still further increased by mixing polymers of formaldehyde along with the solution. None of the colloidal polymers tan as well by themselves as in presence of simple formaldehyde solution. The author inclines to the view that the aqueous formaldehyde solution, reacting as methylene glycol, has a peptising action on the polymeric compounds.

Traube's B-gelatine gives no precipitate with formaldehyde or its polymers. When gelatine solution is treated with formaldehyde and allowed to dry it becomes turbid and exhibits anisotropy.

Dilute acetaldehyde solution has little tanning effect unless alkali is added. The tanning action is increased by adding paraldehyde. Metaldehyde a crystalline polymer, has no tanning effect nor does it increase that of acetaldehyde. Reference is made to Stiasny's work with 2, 3-dioxybenzaldehyde (*Coll.*, 1910, 300) in replying to Nierenstein and Fahrion's claim that there is chemical combination between the aldehyde and the hide substance. The fact that formaldehyde leather is white, similar to formaldehyde and its polymers, and hide treated with 2, 3-dioxybenzaldehyde is yellow like that compound, is in the author's opinion sufficient proof that no compound of the nature of Schiff's base is formed and that no chemical reaction takes place between the aldehyde and the hide but that the aldehydes are present in their natural color.

Formanilide and acetone do not tan. Acetone and alkali have a slight tanning action which is much increased by mixing with condensation pro-

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ducts such as phorone and mesityl oxide. Pelt treated with aldol, carefully washed and immersed in a weak solution of *o*-nitrobenzaldehyde causes the hide to be colored an intense indigo blue throughout. The author claims that this is proof positive that the aldol is not chemically combined with the hide.

Only those aldehydes have a tanning effect which are capable of polymerisation or condensation, which is only the case with aliphatic aldehydes. If the process was merely a chemical reaction there seems no reason why the aromatic aldehydes should not tan as well. They ought to tan better because they have a higher molecular weight. They do not tan because they do not condense or polymerise.

The aldehyde tanning process consists of strengthening the small amounts of peptised substance in ordinary formaldehyde solutions by means of alkali so as to obtain a completely peptised condition.

The Quinone Tannage I. W. MOELLER. *Collegium*, 1918, 71-8; *J. S. L. T. C.*, 1918, 190-191. All kinds of tannages have something more or less in common with the quinone tannage. Fahrion draws a parallel between the quinhydrone formed from quinone and the autoxidation of the fish oil fatty acids. Quinone has been obtained from many materials containing tannins by oxidation. It does not follow that a compound of a quinone character will easily be oxidize or reduced, as Fahrion claims (*Coll.*, 1917, 320). Quinones of high molecular weight do not give up oxygen only to very vigorous reducing agents; *e. g.*, zinc dust and caustic soda.

There is a great deal of evidence which seems to indicate that tannins have a quinone character. Quebracho phlobaphenes when distilled with zinc dust give anthracene and Nierenstein (*Ber.*, 1907) thinks this from rufigallic acid, which is a hexaoxy-anthraquinone. Powarnin found oxyanthraquinone in willow bark tannin. Körner found that by passing air into an aqueous solution of quebracho tannin, phlobaphenes were obtained which differed very little in their chemical composition from the tannin. This is due to the phlobaphenes being there all the time in the quebracho solution and only separating out because of the oxidation of the peptiser to dark colored humins.

The author thinks that the amorphous brown compounds obtained by oxidizing or heating pyrogallol (*Procter, L. I. L. B.*, 115, 120) are related to, if not identical with those products obtained by oxidizing quinone in aqueous solution and which give rise to the tanning effect of quinone. By disturbing the peptiser through oxidation in a vegetable tanning extract solution, the colloid-chemical character of the solution is also changed. A large part of the peptised phlobaphenes is precipitated along with the dark colored humins, which are absorbed by the phlobaphenes causing darkening. The very readily soluble peptiser is converted into a colloidal substance very similar to the phlobaphenes. An intermediate product of this oxidation is always benzoquinone, the quinhydrone of which colors

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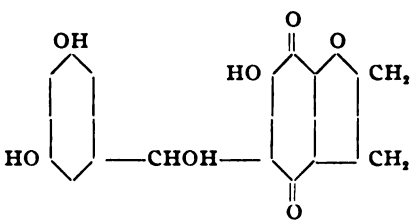
the solution an intense red, to which may be attributed the color of the phlobaphenes.

Nierenstein in his theory of phlobaphene formation concludes that phlobaphenes contain an anthraquinone nucleus, which however is one of those quinones only oxidized or reduced with difficulty. The behavior of different tannins in the Löwenthal method of oxidation is no guide as to their constitution. On adding permanganate to quinone, humins are formed and there is no doubt that in this oxidation process, a certain connection exists between the hydroquinone and the conversion to humic acids. The quinones are formed as intermediate products by the oxidation of the peptiser of the vegetable tannin colloids.

Catechin contains a coumarin nucleus. By methylation a *p*-quinone, catechonetrimethylether, is obtained. This seems to indicate the possibility of quinone formation by the oxidation of the catechin in plants. The easily decomposed peptiser, which consists of compounds easily split off from the polyphenols, is converted into humins whilst quinones containing several nuclei are more difficult to decompose. In tanning with gambier and catechu, the effect is not due to catechin, but to dark polymers of catechin--quinhydrones:



Bodies of a quinone character possess the property of forming colloidal peptised solutions to a high degree.

Fats and Fatty Acids from Petroleum. R. J. Moore and G. Egloff. *Oil Paint and Drug Reporter,* April 29, 1918, 59-60; *J. S. L. T. C.,* 1918, 192. The authors review the numerous articles which have already appeared concerning the conversion of hydrocarbons into fatty acids. There appear to be four methods open to further investigation:—

1. Through halogenation of aliphatic hydrocarbons.
2. By way of Grignard's reaction.
3. By way of naphthenes.
4. Through direct oxidation of paraffins or olefines.

Through Halogenation.—The simplest method of converting hydrocarbons into fatty acids might be by substituting a methyl group by a carboxyl group. Thus, hexadecane $CH_3(CH_2)_{14}CH_3$ might be oxidized to palmitic acid $C_{15}H_{31}COOH$. Halogen derivatives of the paraffin series of hydrocarbons can be produced by mixing the oil and halogen in the dark, vaporizing and subjecting the mixture to the action of a silent

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electric discharge (Eng. Pat. 5,125, 1912). Other methods are also described.

By Grignard's Reaction.—Zelinski (U. S. Pat. 1,012,149) chlorinated petroleum, dissolved it in ether and treated with metallic magnesium and a catalyst. The magnesium compound was then decomposed with a current of carbon dioxide. The fatty acids were then liberated by dilute acids.

By Way of Naphthenes.—The production of glycerides from naphthenic acids is readily accomplished but the resultant fats are in some respects different from the natural glycerides. Naphthenes also lend themselves to Grignard's reaction.

Direct Oxidation of Paraffins and Olefins.—The oil, in the presence of water, is mixed with sodium or hydrogen peroxide. The mass on continued stirring thickens with the production of fatty acids (in the form of soap). The reaction is promoted by heat under pressure. (*Benedix.*) Direct oxidation of paraffin wax can be carried out by heating with a blast of air or oxygen for a prolonged period at 100° C. to 120°C. Mercuric oxide can be used as a catalyst. About 80-90 per cent. of the paraffin wax can thus be converted into fatty acid.

A Volumenometer. J. S. Rogers and R. W. Frey. *J. I. E. C.*, 1918, pp. 554-555. None of the numerous types of mercury displacement apparatus for measuring volume are suitable for large pieces of leather. The apparatus described contains some new features, one of them being the use of a rectangular tank for immersion purposes instead of a cylinder or sphere.

The immersion tank and its cover are of cast iron with accurately ground fitting surfaces so that they can be tightly clamped together. This tank contains a chamber 8 by 1⅛ by 3½ inches. This chamber continues into the top where it converges to a small opening into which a thistle tube is cemented. The top also contains posts to which the pieces to be measured are fastened. A metal tube passes through the bottom of the tank and is connected on the outside to a heavy capillary glass Y-tube fitted with mercury sealed stopcocks. One end of the Y-tube is connected with a reservoir bulb and the other with a burette, both connected with the vacuum system. An ingenious arrangement consisting of graduated glass sleeves below the reservoir bulb and below the thistle tube helps to adjust changes in the zero point. The apparatus is filled with mercury and when the zero points have been fixed the reading is taken on the burette. Some of the mercury is then pumped up into the burette and the bulb and a piece of leather put into the tank which is again sealed and the mercury from the bulb and from the burette if necessary allowed to flow until zero is reached on the scales.

The increase of mercury in the burette is the volume of the leather. All metallic parts are coated with bakelite to protect them from the mercury. A piece of hard rubber which can be checked in water is used to standardize the apparatus. Concordant and reasonably accurate results have been obtained.

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Determination of Water in Soaps. RALPH HART. *J. I. & E. C.*, 1918, page 598. The author recommends the addition of oleic acid or red oil to the xylene in the distillation method for the determination of water in soaps. The amount added should be about the same volume as the soap. This addition increases the accuracy by keeping the soap-xylene liquid more fluid and shortens the time of the distillation by hastening the solution of the soap in the xylene, and by eliminating the foaming that so frequently occurs.

The Use of Sodium Sulphate in the Kjeldahl-Gunning Method. C. T. DOWELL and W. G. FRIEDEMAN. *J. I & E. C.*, 1918, page 599. The authors show by numerous analyses that either anhydrous or hydrated sodium sulphate may be used in the Kjeldahl-Gunning method in the place of potassium sulphate. In their experiments they use 5 grams instead of 10 grams.

Chilean Tanning Industry. SPECIAL AGENT H. G. BROCK. *Commerce Reports* The tanning industry in Chile has reached a higher state of development than in any other west-coast country. It has been tremendously stimulated by the high price of imported upper leather and recently by the increasing difficulties of obtaining the same. All of the sole leather used in the domestic shoe manufacturing industry is produced in the country. Indeed, for many years prior to the war Chilean sole leather was exported in large quantities, chiefly to Germany. Within the past 5 years—more especially within the last 18 months—there has been a distinct improvement in the quality of the box calf and glazed kid turned out by local tanneries.

There are few countries which possess tanning materials in the same abundance as Chile. Lingue bark is the best-known tanning agency, and enormous quantities exist in the forests of the southern Provinces. The supply is said to be inexhaustible. German colonists in the neighborhood of Valdivia and Llanquihue were the first to take advantage of the tanning properties of the Lingue tree to any considerable extent. Once its value had been demonstrated, the tanning industry developed rapidly, until a considerable export trade in sole leather sprang up. A few years after Lingue bark was first employed, another tanning material was discovered in the bark of the Ulmo (elm) tree, which grows almost as extensively as Lingue in the southern sections of the Republic. The fruit of the carob tree is also used to some extent.

Several factories for the manufacture of tannin from Ulmo bark have existed in Valdivia for about 10 years, and previous to the war a considerable portion of the total output was exported to Germany and France. The more important Chilean tanneries are owned by foreigners, French and German nationalities predominating.

The character of the tanning establishments in the southern districts around Valdivia and Llanquihue is distinct from that of the tanneries in the north and central districts. The latter, in normal times, produce sole leather and upper leather chiefly for domestic consumption, while the

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former for a good many years have concerned themselves principally in the preparation of sole leather for the export trade. Before the beginning of the war in Europe the tanneries in the northern and central sections had already begun to seriously feel the competition from imported leather. The tanneries in the southern districts, although they had lost a considerable portion of their former trade with Germany, were still exporting a large quantity of sole leather to the Hamburg market.

Danish Chrome Tannage Materials. *Commerce Reports.* Before the war Denmark imported almost all of its chrome alum and chrome potash, principally from Germany, and when this import was stopped it meant great damage to the chrome leather manufacturers. Iwan Clausen, an engineer connected with the Jorgen Winther Chrome Leather Factory, of Roskilde, Denmark, has now invented a process by which the indispensable chrome materials may be extracted from chrome ore. This is done by means of big ovens in which the crushed ore is burned at a white glowing heat, and then subjected to further treatment. This Roskilde factory is now supplying the whole chrome sulphate consumption of the Danish leather industry.

The chrome ore is obtained from Norway, where it is found in large quantities, especially in Romsdalen, and it is one of the materials coming under the exchange of goods between Norway and Denmark.

New Process of Preparing Hides in Brazil. VICE CONSUL RICHARD P. MOMSEN, Rio de Janeiro, Apr. 22. *Commerce Reports.* This consulate general has been approached by a large Brazilian exporter of hides with a view to introducing into the United States hides that are to be prepared according to a new process for export. In a statement made by the company the following advantages are described for the specially prepared hides as compared with the wet salted or dried hides prepared in the usual manner:

That the resistance is greater; that a period of only eight days is required for preparation before shipment in an absolutely dry condition; when tanned, the hides yield a good sole leather besides pieces of scrap leather from each side of the hide; the hide treated by this process is odorless and required no special shipping facilities, the obnoxious qualities which makes the shipment of hides on passenger vessels impossible, being eliminated; the weight is 56 per cent. less than that of wet salted hides, making their shipment much cheaper; it requires about 75 hides to the ton, whereas in the case of wet salted hides the average is but 33 hides to the ton; the special treatment makes the hides immune to attacks from insect pests, and all animal germs are killed in the process.

Small samples of hide treated with this process are transmitted, and the firm will, upon application, send samples and further details to American firms interested in this subject.

[The firm's address can be obtained from the Bureau of Foreign and Domestic Commerce or its district of co-operative offices by referring to file No. 102180. The samples referred to can be examined at the bureau or its district offices by referring to the same file number.]

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Norwegian Demand for Tanning Material. *Commerce Reports.* Only half of the Norwegian production of hides can be used for sole leather, and a great deal of raw material has been imported for this purpose. On the other hand, lighter hides, such as calf and sheep skins, have to a great extent been exported. After having been treated in foreign tanneries they have been repurchased. The Norwegian tanneries have only been equipped for treating a small part of the lighter kinds of skin of the country's own production.

Now, however, the State Leather Central is making investigations with regard to how much of the Norwegian production of lighter hides their tanneries for upper are able to treat; also whether the sole leather tanneries can reorganize their production in such a way that they will also be able to tan uppers, and to what extent. It is the intention to help themselves as much as possible. In order to accomplish this, Norway must have tanning material. Everything depends on this. The State is therefore taking steps to organize the production of tanning bark.

The whole Norwegian tanning industry was before the war based on import. The tanning material needed, about 10,000 tons, cost so little that it paid to import it even from such distant places as India and Brazil. This import has now been entirely stopped. The agreement with America stipulates hardly any fixed quantities of tanning material. The stocks on hand will hardly last more than three or four months. Everything taken into consideration, Norway must therefore try to procure as much as possible of Norwegian tanning bark. Beyond the 10,000 tons, about 2,000 tons have been produced at home. However, the Norwegian bark contains only one-fourth the tanning material contained in the bark imported, so four times as much will be required; that is, 40,000 tons. It is doubtful whether this quantity will be reached this year, but it is hoped to get a good part of it.

In order to gather as much bark as possible, a high price is offered for it—for air-dried spruce bark 20 ore (100 ore [crown] equals $0.268 American currency), for birch bark 24 ore, for oak bark 28 ore, and for willow bark 22 ore per kilo (2.2 pounds), delivered at the nearest railroad station or steamship pier. On account of the high freight the prices for the districts north of Trondhjem will be 3 ore lower per kilo.

Only bark from the trees hewn in "Sevjetiden" (sap time) can be used.

The gathering of bark will not damage the forests, because the bark is taken from hewn trees. Formerly it was simply left as refuse. That it has now become of value means an extra income for the timber owners of 30 to 40 crowns per dozen hewn timber, which means that the owners practically get their timber hewn for nothing. It is expected that mainly spruce bark will be gathered—bark of cellulose timber. In contradistinction to saw timber, which must be treated in another way in order to not to crack, the cellulose timber may be cleft at once. In the Sorland district, where for several generations stub cultivation has been carried on with a view to oak bark production, the high price of bark will probably mean

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an increase in the income of the small cultivators. By stub cultivation the tree is hewn and root shoots are cultivated on the stub. When the young shoot has reached a certain height, it is hewn and cleft. On the whole, the bark of the young trees is richer in tanning material than that of older trees.

In connection with the bark gathering plans are being made for building an extract factory for tanning material. If this is realized, it will probably also be possible to utilize the bark of winter-hewn trees. In that case the method of the chemist, Hans Landmark, will probably be used. This is a chemical process by which the winter bark of spruce trees is given an addition of the sugar which is only found in the bark in "Sevje" (sap) time. Statistics from 1910 show that in peace times Norway imported 63,000 crowns' worth of spruce bark extract per annum. Many tanners believe that the winter bark is less valuable because of a lower content of tanning material. Mr. Landmark does not share this opinion, but believes that the tanning material contents of the bark are about the same the year around.

A Norwegian tanning material, "Norvego," a sulphite cellulose extract, which is made by the Union Co., has been used considerably in Denmark and Sweden. In Norway the opinions of the tanners differ somewhat with regard to this material. Better results seem, however, to be obtained in tanning uppers than in tanning sole leather. The result depends somewhat on the mixture proportion of "Norvego" with other tanning materials. It is reported in this connection that the Union Co. intends to send out men to the tanneries to teach them the right use of "Norvego," which, when used with various other chemicals, has the effect of causing the hides to more easily absorb the tannin from the other tanning materials.

Principles of Extraction of Tanning Materials. E. G. KEINER. *H. & L.*, Aug. 17, 1918. There seems to be a difference of opinion as to whether the closed or the open extraction is preferable. Many large concerns are extracting in open vats, and obtain very satisfactory results. The disadvantage, however, seems to be that the expense of extraction is very high on account of heat lost, as well as the high cost of labor. The closed system has been used in Europe for extracting most extensively with very much success.

The principle of the extraction is based on the so-called diffusion. If a dry tannin material is put into a thin liquor or water it will be soaked full with liquor. In this liquor the water solubles of the tannin material will go into solution, which means within the material a saturated liquor will originate. This liquor within the material will now equalize with the liquor outside of the material, and the liquor within the material will become thinner and the liquor outside will become stronger. It is very interesting to follow this operation, as upon this principle all the extractions and manufacture of liquor is based. As the liquor inside of the tannin material, as well as outside is equally strong, the procedure begins anew,

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as soon as the liquor outside of the material has been removed and replaced by the thinner liquor or by water.

The small amounts of tannins and non-tannins that are contained in the tannin material as yet insoluble are going into solution gradually in the same proportion as the liquor within the tannin material becomes less concentrated. This method will be favored by the way that the solubility of the substances in question is increased. For this purpose heat comes into consideration almost exclusively in a tannery. Chemical substances that increase the solubility are seldom or not at all used. Alkali especially will do the work, but that makes it dark.

From the description of the extract process it is seen that the movement of the tannin material, as far as it is caused by pumps, cannot increase the extracting effect, but it will only cause a quickening of the extracting process. Movement, therefore, will give good results always where time is valuable and has to be saved, meaning to say where the extract manufacturer cannot wait until the equalizing of the liquor takes place by the law of diffusion.

The movement of the tannin material also causes a quickening of the extraction without increasing the full extraction effect. The results change somewhat if a movement of liquor and tannin material is used. In Europe a so-called riedersche automat was used and according to this automat the same liquor does not come back to the old tannin material, but a continuous change takes place by which the tannin material is moved into thinner liquor in the same way as it is extracted. These seem to be really the ideal conditions for extracting.

From the description of the extracting process we learn further that the extraction of the tannin takes place better and quicker the greater the difference is between the consistency of the liquor outside of the tannin material compared with the concentration of the liquor contained within the tannin material.

From this the conclusion is drawn that the practical tanner should pump the best liquor from his extraction as completely as possible. In this connection it is of interest to note the temperature under which the extraction proceeds most favorably.

Oak bark	80° to 90° Centigrade
Spruce bark	80° to 100° Centigrade
Mimosa	70° to 80° Centigrade
Valonia	60° to 70° Centigrade
Myrobalans	90° to 100° Centigrade
Sumac	50° to 60° Centigrade
Quebracho	80° to 90° Centigrade
Divi divi	50° to 60° Centigrade

However, these figures are not so very important to the practical man.

During the extraction process tanning materials are gradually brought in contact with a warmer liquor. In consequence the easily destroyable and easily soluble tannins and non-tannins are usually already in solution

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when the material comes in contact with a higher temperature. However, it is dangerous to use too high a temperature, as tannin in high temperature will be destroyed. High pressure caused by too much heat is therefore to be avoided, while a pressure by pressed air without overheating is of great advantage.

The pressure caused by air is cheaper than by steam. However, no matter which system is used, too much movement of the liquor should be avoided if the pumping and warming is done at the same time. In such a case an oxidation of the tannin will take place under most favorable conditions if it is brought into solution and warmed at the same time, and as a consequence of which such liquors are very dark.

The advantages of the closed over the open method of making extract are that they are easier and better worked. In a closed extraction the movement of the liquor is caused by pressure, in the open by pumping. It is much easier to remove the hot liquor by pressing than by pumping.

A second advantage is the fact that the liquor, by pressing, is much cleaner than if it is pumped. In the closed extraction a much more concentrated liquor is obtained. Much less steam is necessary in the closed extraction than in the open. The saving of steam has been proven to be 30 to 40 per cent. The color of the liquor in a closed extraction is much better than in the open, inasmuch as the liquor does not come so much in contact with air.

So far as the expenses are concerned the closed extracts are more expensive. The repair expenses are less in a closed extraction.

At the present time there are two quebracho extracts treated with sulphite on the market and the grade depends upon the amount of insolubles the ordinary quebracho contains. There are moderately and highly treated quebracho extracts on the market, the highly treated having hardly any solubles.

Blood cleared quebracho extracts are seldom found on the market to-day on account of the war conditions. The treating of the quebracho extract is done by adding liquid bisulphite under heat and pressure and continuous stirring. It is claimed that the pressure is necessary in order to obtain a thorough effect.

A Simple Leaching System. A TANNER. *La Halle aux Cuirs*, June 16, 1918, p. 213. For the benefit of one of his readers who found himself in the predicament of being unable to obtain enough extract, although plenty of bark was available, the writer describes the following system which he himself had used some years ago. Six large wooden vats with double bottoms were joined by pipes leading from the bottom of one to the top of the next. They were placed upon a platform sufficiently elevated to permit a small truck to pass underneath for carrying away the spent bark. A special arrangement permitted drawing off the liquor from any vat, since each in turn became the head or tail vat of the system. In this region at the time, the low price of bark permitted the luxury of operating the system with cold water and the consequent loss in tannin

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was compensated by a very clear color, making a suitable liquor for white calf and sufficiently strong for light skins. More tannin is extracted by hot water, but certain precautions are necessary which tanners sometimes overlook. For oak bark a temperature of 80°C. must not be exceeded, because although boiling water dissolves certain tannins not very soluble in cold water, it likewise dissolves coloring matters and non-tannins injurious to the leather. The system described is to be used rather as an emergency measure. It is hardly suitable for use with heavy stock since it does not furnish liquors sufficiently concentrated, nor would it be practical for use in a large tannery because a system of enormous proportions would be required. J. A. W.

The Normal Composition of Chestnut Extract. ANON. *La Halle aux Cuirs,* June 16, 1918, p. 213. Normal chestnut extract as delivered to the tanner should contain 26 per cent. tannin (shake method) and only such other matters as were actually extracted from the wood. The color by the tintometric method should be about 4 of red. J. A. W.

Slate Vats. ANON. *La Halle aux Cuirs,* June 16, 1918, p. 214. It may be useful to know the opinion of Mr. Seymour-Jones, president of the International Commission for the Conservation, Preparation, and Disinfection of Hides and Skins With Hair, in regard to the employment of slate vats. He believes that tanners will readily see that vats of slate are much to be preferred to those of brick or wood, being more easily cleaned and therefore available for use with all kinds of liquors. No iron parts should be allowed to come into contact with a liquor. J. A. W.

Chrome Sores. A TANNER. *La Halle aux Cuirs,* June 30, 1918. The writer doubts the existence of an eczema peculiar to those handling bichromate liquors. He believes that this local irritation manifests itself only upon such persons as are subject to it whenever the skin comes into contact with any irritating substance, either powdered or dissolved, whatever that substance may be. Of the restaurant employees who are charged with plunging dishes into solutions of lye or caustic soaps, those who are liable to the affection are soon compelled to abandon the work because of the appearance of an eczema which the writer regards as not essentially different from chrome sores. In any case the affection apparently disappears when the skin is no longer brought into contact with the irritant.

The Mechanism of Vegetable Tannage. A TANNER. *La Halle aux Cuirs,* Aug. 4, 1918. (A comment upon and summary of a recent paper on this subject by Professor Meunier in *Chimie et Industrie,* an abstract of which will appear in a later issue.) Vegetable tannage may be considered as the result of two actions: the *first* being chemical combination between the hide substance and products analogous to quinone contained in the tan liquors, and the *second,* adsorption which is at first reversible but is followed by a partial transformation to the irreversible and stable form. In slow tannages chemical action and irreversible adsorption are much more marked than in rapid tannages as shown by the resistance of

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the leather to the prolonged action of water. In rapid tannages the leather often yields as much as 30 parts of water soluble matter per 100 parts of absolutely dry leather as against less than 14 parts for slow tannages, which are therefore to be preferred. The quality of the leather is also greatly influenced by the nature of the tanning materials; their richness in quinone-like substances, the sensitivity of the tannins to adsorption, the ease with which they become irreversibly adsorbed, all vary with different materials, which makes proper choice an important matter.

J. A. W.

Substitutes for Leather Soles. LEONARD ETHERINGTON. *Printers Ink, through H. & L.*, Aug. 17, 1918. A discussion on the uses of substitute leathers particularly, fiber substitutes for soles.

PATENTS.

Machine for Treating Hides and Skins. U. S. Patent 1,261,534. H. A. HOLDER, assignor to W. F. Fitzgerald, Lynn, Mass.

Imitation Leather. U. S. Patent 1,262,132. W. O. STODDARD, JR., assignor to Duratex Co., Newark, N. J. A textile fabric coated with a solution of nitro-cellulose to which may be added a blown vegetable oil film, a fabric, and materials imbedded in such a film to reinforce same.

Treating Waste Waters. U. S. Patent 1,263,532. C. E. CUMMINGS, assignor to Eastern Tanners Glue Co., Gowanda, N. Y. Consists in passing carbon dioxide through the liquid and removing the precipitate formed.

Leather Substitute. U. S. Patent 1,263,171. E. WEINHEIM, New York, N. Y. Dissolving a filler base in a volatile solvent; admixing an oil, heating in an enclosed vessel, distilling off the volatile solvent, and while still hot and fluid, applying to a body fabric.

Waterproofing Composition. U. S. Patent 1,263,823. V. A. WALLIN, Grand Rapids, Mich., and O. A. HEPPES, La Grange, Ill. A base of a strong fiber and a filler of spent tan bark finely divided crosswise of the grain into pieces so small as to be saturable, felted together in sheet form and a waterproofing material applied to the base and spent bark.

Sewage Treating Apparatus. U. S. Patent 1,264,990. H. H. STEPHENS, assignor to The Sanitation Corp., New York, N. Y.

Water Purification and Softening. U. S. Patent 1,265,346. J. J. LASSEN AND U. F. HJORT, London, England.

Treating Leather. U. S. Patent 1,265,648. E. P. GILLILAND, Norwood, Mass. A method of treating leather by applying a surface coating of a wax, a resin, and a filler, and then coatings of a gelatinious compound.

Method of Tanning. U. S. Patent 1,266,203. G. BOSIO AND A. PERADOTTO, Turin, Italy. Method consists in using a concentrated tanning extract (7 to 35 per cent. tannin) and quickly raising the heat of the extract to the heat of the animal while living.

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Sterilizing Water and Sewage. U. S. Patent 1,266,803. V. HENRI, A. HELBRONNER AND M. VON RECKLINGHAUSEN, assignors to the R. U. V. Co., New York, N. Y. Method consists in passing the liquids through a field of ultra-violet rays.

Leather Working Machine. U. S. Patent 1,267,853. L. F. CUTLER, assignor to The Turner Tanning Machine Co.

Leather Staking Machine. U. S. Patent 1,268,637. F. F. SLOCOMB, Philadelphia, Pa.

Leather Manufacture. U. S. Patent 1,268,876. A. OBSER, Newark, N. J. Tanning in bark liquors, splitting, pickling, re-tanning in a metallic tanning solution, neutralizing, washing, and dressing with a fat liquor.

Artificial Leather. U. S. Patent 1,269,339. T. J. TURNER, assignor to E. I. duPont de Nemours Powder Co. The process consists in coating a fabric with nitro-cellulose by means of calendar rolls.

Waterproofing Leather. U. S. Patent 1,269,658. H. C. TRENAMAN, Hamilton, Canada. A composition of grease 25 per cent., gum 5 per cent., wax 30 per cent., oil 35 per cent. and rubber 5 per cent.

Vegetable Glue. U. S. Patent 1,269,678. V. G. BLOEDE, Catonsville, Md. Made by dissolving starch in a caustic alkali and then partly neutralizing with a gaseous acid.

Drying Patent Leather. U. S. Patent 1,269,931. E. HURTZ, assignor to Cornelius Heyl, Worms, Germany. Treating with ultra-violet rays in an atmosphere of nitrogen or some non-oxidizing gas.

Artificial Leather. U. S. Patent 1,270,055. W. W. RICHARDS, assignor to E. I. duPont de Nemours Powder Co. A pyroxylin coated fabric having the odor of leather and containing an empyreumatic substance, animal oil and essential oil.

Waterproof Glue. U. S. Patent 1,270,477. W. W. WOOD, Tacoma, Wash. A mixture of one gallon silicate of soda, two gallons of blood, three gallons of water and an ounce of spirits of ammonia heated together.

Tanning Hides. U. S. Patent 1,271,060. R. N. MOORE, Thorp Springs, Texas. A tanning solution of two pounds of gum gambier, one-half pound of alum, one pint of vinegar, one ounce fluid extract white oak bark, one ounce fluid extract of poke root and perfume oil.

Sewage Treatment. U. S. Patent 1,271,926. GEORGE MOORE, assignor to The Chemical Process Co., New York, N. Y.

Hide and Leather Working Machine. U. S. Patent 1,272,163. R. F. Whitney, assignor to Whitney Machine Co., Winchester, Mass.

Tanning Process. U. S. Patent 1,273,662. W. PETRIE, assignor to Petrie Process Co., New York, N. Y. The process of tanning hides which comprises agitation with a small but constantly renewed quantity of tanning liquor, the liquor being insufficient to prevent free access of air to the hides.

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Extracting Mangrove Leaves. British Patent 106,815. The leaves are digested with water and the liquor filtered off and concentrated *in vacuo*. Bisulphites and other salts are added and the resulting mixture sold as a dye (Inglotine C.).

Tanning Apparatus. British Patent 113,408. G. D'ANGELO, Turin, Italy.

Leather Making. British Patent 114,358. A. BARCLAY, Prahran, Victoria, Australia. The hides or skins are soaked in a saturated solution of magnesium sulphate to which a small quantity of formalin may be added. They are then immersed in a strong solution of vegetable tanning material.

Tanning. British Patent 114,631. F. GILARDINO, Turin, Italy. Rapid tanning attained by subjecting both sides of the skin to tanning liquor under pressure or one side to a vacuum and one to pressure.

Tanning. British Patent 115,009. VULCAN ENGINEERING CO., Whitehaven, Cumberland, England. The process of reeling hides or skins.

Impregnat Material for Leather. German Patent 302,158. A resin such as Coumarone or Burgundy is heated with animal fat, and sulphur is added to vulcanize the mass.

Leather Substitute. German Patent 302,194. F. KROHMER AND A. SCHATZLE. Leather dust mixed to a paste with a glue adhesive and an oil varnish can be coated on fabric and used to wrap around models to make a form.

Leather Substitute. German Patent 302,329. Successive treatment of skins in two baths, the first a mineral salt such as lead acetate, barium chloride or zinc sulphate, and the second sulphuric acid or a solution of sodium sulphate or carbonate.

Leather from Leather Waste. German Patent 302,330. M. RIGELL, Buda Pest. The waste is treated with an aluminum salt and vegetable tanning material, dried, treated with a soap solution, then a solution of barium chloride. An adhesive is added and the mixture pressed between grooved rolls and finally passed through a tanning solution.

Tanning Hides and Skins. German Patent 303,601. Pyroligneus acid is added to a tanning agent.

Tanning Agent. German Patent 303,640. *Deutsch Koloniale Gerb- and Farb-Ges.* The products obtained by condensing four molecules of formaldehyde with two molecules of α- or β-naphthol monosulphonic acid are further condensed with one molecule of formaldehyde or its equivalent. The new product obtained is more soluble in water.

Leather Substitute. German Patent 304,096. C. JUNG, Reinhart, Austria. Fibrous material saturated with sulphurized oils is mixed with caseinate, sulphur, shellac, and balata and pressed into plates. The product can be used for sole leather. The balata should be from 5 to 15 per cent. of the mixture.

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BOUND VOLUMES.

The publishers of the JOURNAL have been unable to secure leather suitable for binding purposes, and feel that such leather cannot be obtained until some time after the war. The manager has had a limited number of Vol. 12, 1917, bound in cloth and in brown buckram. Members wishing to exchange their unbound numbers for a volume bound in cloth or brown buckram can do so by sending such unbound numbers to the manager at Ridgway, Pa.

There has been such a demand for back numbers that Vols. 7, 8, 9 and 12, 1912, 1913, 1914 and 1917 have become nearly exhausted and by ruling of the Council these volumes can be sold only in complete sets. The attention of the members is called to those numbers needed to fill out complete volumes, which are advertised on the back inside cover of the JOURNAL. The manager is especially anxious to obtain the issue of January, 1913.

ABSORPTION OF TANNIC ACID IN SOLE LEATHER MANUFACTURE.

By Allen Rogers.

A Report from the Tanners School, Pratt Institute.

For the past three years investigations have been conducted at Pratt Institute with the object of obtaining data that would be of aid to the tanner in taking an inventory of his yard. Many points have been studied, and the data thus far submitted has thrown light on several sources of loss heretofore ordinarily overlooked. For instance, in the work of last year, one of the points given considerable attention was the oxidation of tanning materials in the yard. Loss from this cause had never before been considered, at least not with the authority of records. The results subsequently obtained, however, have been so striking that it behooves the tanner to devote attention to this very important matter.

The investigation conducted during the spring and summer of 1917 dealt with the absorption of tanning materials during the various stages of the process, and the data given below indicates

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not only the rate of absorption, but gives a fair idea of the actual amount of tannic acid absorbed by the stock.

Through the courtesy of one of the nearby sole leather tanneries it was possible to obtain samples for analysis, together with information valuable in the interpretation of results. The plan followed was to take samples of leather and liquor at various stages and from the analytical data determine the tannin units taken up by the stock. The process at this plant consisted in a union tannage, and the stock handled was green-salted packer steers.

The stock was pretreated by soaking and liming in the usual manner; and the unhaired and scudded hides were washed and transferred to the cool pool overnight. From the cool pool the stock entered the yard. In order to trace the tannage absorption, samples were taken at various stages—in the rockers, press layers, layers, extract, and loft. From the data given in Table I certain conclusions can be drawn.

TABLE I.—ANALYSIS OF LEATHER SAMPLES.

Sample	Per cent. moisture	Per cent. ash	Per cent. hide sub.	Per cent. tans and non-tans
Cool pool	44.50	1.31	98.00	—
3 days in rockers	53.97	1.03	94.40	4.57
6 days in rockers	42.49	0.55	86.44	13.01
9 days in rockers	40.65	0.38	83.55	16.07
12 days in rockers	50.03	1.59	78.54	19.87
14 days in rockers	27.82	0.63	75.65	23.72
Out of rockers	34.53	1.54	71.00	27.46
3 days in press layers	45.91	0.92	65.55	33.53
8 days in press layers	45.24	0.43	60.28	39.29
13 days in press layers	37.09	0.36	57.37	42.23
20 days in press layers	36.02	0.32	54.97	44.71
7 days in 1st layer	37.29	0.28	53.97	45.75
12 days in 2nd layer	37.37	0.39	53.60	46.01
26 days in 3rd layer	20.60	0.79	49.06	50.15
Out of 3rd layer	25.57	0.53	47.31	52.16
Out of extract	13.88	0.56	46.96	52.48
Out of temp. pit	24.42	0.54	48.43	51.03
Out of bleach	26.23	0.39	51.12	48.49
From oil wheel	32.68	1.04	49.23	49.73
From loft	17.46	1.00	48.55	50.45
After rolling	15.09	0.78	48.40	50.82

It will be seen from the foregoing table that over half the tannage was accomplished during the fifteen days in the rockers;

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and further that after thirteen days in the press layers the tannage had reached over four-fifths of the total absorption. Thus, by this process, it took sixty-two days more for the stock to absorb the remaining fifth of the tanning material.

In order to appreciate the relation of dry weight to wet weight, Table I when calculated to the wet basis gives the data shown in Table II.

TABLE II.—ANALYSIS OF LEATHER SAMPLES, WET BASIS

Sample	Per cent. moisture	Per cent. ash	Per cent. hide sub.	Per cent. tans and non-tans
Cold pool	44.50	0.73	54.37	—
3 days in rockers	53.97	0.47	43.45	2.10
6 days in rockers	42.49	0.31	49.71	7.48
9 days in rockers	40.65	0.25	49.58	9.53
12 days in rockers	50.03	0.78	39.25	9.93
14 days in rockers	27.82	0.45	54.60	17.12
Out of rockers	43.53	1.00	46.48	17.98
3 days press layers	45.91	0.50	35.45	18.13
8 days press layers	45.24	0.23	33.00	21.52
13 days press layers	37.09	0.23	36.09	26.56
20 days press layers	36.02	0.19	35.17	28.60
7 days first layer	37.29	0.17	33.84	28.68
12 days second layer	37.37	0.24	32.56	28.81
15 days third layer	30.93	0.56	33.23	35.26
26 days third layer	20.60	0.62	39.03	39.82
Out of 3rd layer	25.57	0.39	35.21	38.82
Out of extract	13.88	0.48	40.44	45.21
Out of temp. pit	24.42	0.41	36.60	38.57
Out of bleach	26.23	0.29	37.71	35.77
Out of oil wheel	32.68	0.70	33.14	33.47
Out of loft	17.46	0.82	40.07	41.64
After rolling	15.09	0.66	41.09	45.15

The amount of tannic acid in the yard liquors was determined by samples taken for analysis. The results of these tests are shown in Table III.

The hides, it will be seen, entered the liquor at 23° Bk., containing 1.10 per cent. of tannic acid and 4.15 per cent. of non-tans. The head liquor stood 33° Bk. and contained 2.73 per cent. of tans with 4.57 per cent. of non-tans. Therefore, the sappage in fifteen days was 10° Bk., the absorption of non-tans 0.45 per cent., and the absorption of tannic acid 1.63 per cent. In this tannery the volume of liquor in the rockers was 76,620 cubic feet, or, at 62½ pounds to the cubic foot, there were 4,865,370 pounds.

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In this volume of liquor the sappage of tannic acid was 79,305.53 pounds. The capacity being 384 hides per day gives a total of 5,760 hides in process in the rockers. The pounds of tannic acid absorbed divided by the number of hides shows that each hide took up 13.77 pounds of tan.

TABLE III.—ANALYSIS OF LIQUORS

Sample	Total solids	Soluble solids	Non-tans	Tans	Barkometer	Acid
Tail rocker	5.68	5.25	4.15	1.10	23	0.27
Head rocker.....	7.88	7.30	4.57	2.73	33	0.45
Spent tail press ...	7.36	7.27	5.16	2.11	31	0.30
Spent head press .	10.63	8.71	4.63	4.08	43	0.30
Fresh tail press ...	8.37	7.91	4.86	3.05	35	0.33
Fresh head press..	10.92	9.14	5.02	4.12	42	0.39
Tail 1st layer	9.49	8.76	4.67	4.09	40	0.33
Head 1st layer ...	10.87	10.05	5.24	4.81	46	0.36
Tail 2nd layer	10.43	9.61	5.16	4.45	42	0.27
Head 2nd layer ..	10.66	9.77	5.13	4.64	45	0.27
Tail 3rd layer.....	12.88	12.53	4.79	7.74	53	0.36
Head 3rd layer ...	15.11	14.60	6.38	8.22	62	0.36

Analyses of the hides at the various stages indicate that the absorption of tannic acid was 17.98 per cent. The hides entering the rockers weighed about 65 pounds each, but, on account of the absorption of tannic acid, they increased to about 75 pounds each. Using the head rockers' weight to check up the analytical results, we have

$$\frac{79{,}305.53 \times 100}{437{,}760} = 18.12 \text{ per cent.}$$

of tannic acid absorbed. The slight difference between the tannic acid estimated from the strength of liquors and that found by analysis is within reasonable limits. The value of this data lies in the fact that it serves as a check on the amount of material found in the liquor and the amount taken up by the hide. Knowing the quantity of tanning material originally employed, it is a simple matter to determine any loss that may occur during the process.

Assuming that each tannin unit is valued at 7¢, it is possible to estimate the cost per 100 pounds, or cost per hide, to put the stock through the rockers. Thus, from the above data we may say that each 65-pound hide takes up 13.77 pounds of tannic acid, which, at 7¢ per pound, amounts to $1.26 per hide. With a

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capacity of 384 hides per day, the rocker value of tannin units absorbed by the stock is $485.37.

For the twenty days that the stock remained in the press layers the sappage was 11° Bk. with an absorption of 2.01 per cent. of tannic acid. The capacity of the press layer being 29,847 cubic feet with a liquor weight of 64½ pounds per cubic foot gives a total weight of liquor of 1,822,068 pounds. As the loss of tannic acid is 2.01 per cent., it shows an absorption of 36,623.5 pounds. The press layers contain 7,680 hides, which means an absorption of 4.75 pounds per hide. This absorption, calculated on the tannin unit shows a cost of 31¢ per hide, or $121.92 per day.

The analysis indicates a sappage of from 46° to 40° Bk. in the first layer for the seven days consumed. The amount of tannic acid absorbed is shown to be 0.72 per cent. As the capacity of the first layer pits is 9,680 cubic feet with a weight of 64.6 pounds to the cubic foot, the total weight of liquor sapped is 625.425 pounds. With a decrease of 0.72 per cent. on the liquor, we have a total absorption of 4,502 pounds for the 2,688 hides in process, or 1½ pounds per hide. This amounts to 576 pounds per day, and at a value of 7¢ is equivalent to a cost of $40.32 for the 384 hides or 11½¢ per hide.

The analysis of the liquor from the second layer shows a sappage of from 45° to 42° Bk. during the twenty days in process, with an absorption of 0.19 per cent. of tannic acid. As the capacity of the second layers is 11,660 cubic feet with a weight of 65 pounds to the cubic foot, the weight of liquor is 757,900 pounds. With a sappage of 0.19 per cent. on the amount of the liquor, we have 1,440 pounds of tannic acid absorbed by the 4,608 hides in process, or 0.31 pound per hide. The analysis of the head and tail pits, however, represents the tannic acid absorbed by a pack going through the layers, and so should be calculated on the 384 hides daily capacity, or this would mean that the 384 hides had absorbed 1,440 pounds of tannic acid, which would be equivalent to 3¾ pounds per hide. At a cost of 7¢ per unit, the value of tan absorbed per hide would be 26¢. This would amount to $100.80 per day.

The analysis of the liquor from the third layer shows a sappage from 62° to 53° Bk. during the thirty-five days in process, with an absorption of 0.48 per cent. of tannic acid. As the capacity

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of the third layer is 16,720 cubic feet with a weight of 65 pounds to the cubic foot, the weight of liquor is 1,097,668 pounds. A sappage of 0.48 per cent. on the amount of liquor is equivalent to 5,268.8 pounds of tannic acid absorbed. As there are 13,440 hides in process, it means a distribution of 0.39 pound per hide. At a cost of 7¢ per unit, this amounts to 0.0259¢ per hide in process. The cost per hide, therefore, of putting stock through the yard is as follows:

Rockers	$1.264
Press layers	.3175
1st layer	.1125
2nd layer	.2600
3rd layer	.0264
Total	$1.9804

The analysis of the head and tail liquors, however, represents the amount of tannic acid absorbed by a series of packs going through that layer, hence, if calculated on the 384 hides daily capacity, the absorption would be 161.5 pounds, or 0.45 pound per hide.

An attempt was made to determine the amount of tannic acid absorbed from the extract and tempering pits, but the results were so unsatisfactory that they were not recorded. Analyses of hide samples were made, and, although the averages are given, it is hardly possible to draw any conclusions from them. It is very apparent, however, that there is a loss of tanning material in the tempering pits and bleach, but this loss does not enter into the cost of tanning, except that it is lost weight which cannot be sold. This cost represents only the actual tannic acid absorbed during the process and does not include that taken up during extracting and tempering. Neither does it account for non-tans, which are absorbed, nor for loss due to other causes.

Some of the losses of tannic acid were next considered, and it was thought that possibly there might be some variation in the content of tannin depending upon the condition of sampling. To prove this, a series of samples were taken from the top, middle, and bottom of a number of pits, and analyses of the liquors carried out under identical conditions.

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TABLE IV.—ANALYSIS OF LIQUORS

Sample	Total solids	Soluble solids	Insoluble solids	Tans	Non-tans
Tail rockers	6.40	3.79	2.61	1.13	2.66
Head rockers	6.04	5.88	0.16	3.57	2.31
Tail press layer top	5.82	5.72	0.10	2.67	3.05
Tail press middle	5.72	5.80	0.02	2.81	2.99
Tail press bottom	5.87	5.83	0.04	2.75	3.08
Head press top	10.76	7.14	3.62	3.12	4.02
Head press middle	7.06	7.02	0.04	3.56	3.46
Head press bottom	9.54	6.92	2.62	3.62	3.30
1st layer spent, top	7.93	7.91	0.02	3.86	3.95
1st layer spent, middle	8.06	8.02	0.04	3.82	4.20
1st layer spent, bottom	8.12	7.93	0.09	4.12	3.81
1st layer fresh top	8.49	8.40	0.09	4.67	3.73
1st layer fresh, middle	9.07	8.38	0.69	4.59	3.79
1st layer fresh, bottom	9.15	8.83	0.22	5.03	3.80
2nd layer spent, top	8.95	8.82	0.13	4.39	4.43
2nd layer spent, middle	8.88	8.87	0.01	4.55	4.32
2nd layer spent, bottom	8.01	8.85	0.16	4.83	4.02
2nd layer fresh, top	9.07	8.97	0.10	4.76	4.21
2nd layer fresh, middle	9.78	9.33	0.45	4.93	4.40
2nd layer fresh, bottom	9.92	9.92	0.00	5.04	4.88
3rd layer spent, top	10.93	10.81	0.12	6.54	4.27
3rd layer spent, middle	11.81	11.42	0.39	6.69	4.73
3rd layer spent, bottom	11.89	11.73	0.16	7.62	4.11
3rd layer fresh, top	14.72	12.59	2.13	8.04	4.55
3rd layer fresh, middle	12.85	12.69	0.16	7.96	4.73
3rd layer fresh, bottom	13.12	12.72	0.40	8.17	4.55

The foregoing results are very interesting and instructive, because they show a condition which is never taken into account when making an inventory, namely, that of the higher content of the bottom and middle liquors. Should this difference be calculated into cost, the amount would be a considerable item.

One source of loss in an extract yard, or even in a bark yard, is from the discard of sludge. To determine the amount of waste, analyses were made of the sludge from the extract house and rocker pits. Table V gives the data that was obtained.

The results obtained are somewhat different than had been expected, but show that the settlings contain as much tannin as the liquors. As these settlings constitute what is known as sludge from the cooler, it was thought well to make a test of the sludge liquor from the sludge pit. The results of these analyses are shown in Table VI.

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TABLE V.

Sample	Total solids	Soluble solids	Insoluble solids	Tans	Non-tans
Liquid Oak Extract					
Upper portion	7.19	7.05	0.14	3.23	3.82
Settlings	7.35	7.09	0.26	3.47	3.62
Solid Quebracho Extract					
Upper portion	5.93	5.67	0.06	4.10	1.48
Settlings	6.23	5.42	0.81	3.91	1.51
Liquid Chestnut Extract					
Upper portion	6.22	6.74	0.05	4.46	2.33
Settlings	7.92	6.95	0.97	4.15	2.80
Liquid Hemlock Extract					
Upper portion	7.96	7.06	0.90	3.86	3.18
Settlings	9.23	7.57	1.76	3.81	3.76
Myrabolans					
Upper portion	7.05	6.95	0.10	3.67	3.28
Settlings	9.94	7.58	2.36	3.44	4.14

TABLE VI.—ANALYSIS OF SLUDGE

Sample	Total solids	Soluble solids	Insoluble solids	Tans	Non-tans
1st layer cooler	24.14	14.59	9.55	6.14	6.45
Cooler sludge No. 1	24.01	14.11	9.90	6.24	7.87
Cooler sludge No. 2	31.34	12.91	18.43	9.49	3.42
Liquid from pit	3.06	2.97	0.09	2.06	0.91

The conclusion to be drawn from the work is that a sample analysis of yard liquors is not a sufficient basis for calculating a complete cost system. It indicates that there are losses in various places which must be taken into consideration. It also shows that the degree of tannage is not subject to a mathematical calculation, and the yard should never be considered as half tanned.

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SHARK SKIN LEATHER.

By Allen Rogers.

A Report from the Tanners School, Pratt Institute.

From time immemorial the manufacture of leather has been confined almost exclusively to the tanning of skins and hides of domestic animals, and the supply from this source has always been found adequate to meet the demands of the consuming trade. Within the past few years, however, the supply of raw material has become limited, and so many ways and means of conservation have been suggested. Among the various ways suggested for increasing our leather supply, the tanning of fish skins is prominent. In order to determine the feasibility of the suggestion the writer undertook an investigation along this line. During the fall of 1917, through the courtesy of the Bureau of Fisheries, a large number of shark skins were obtained. These skins were secured from various sources and consisted of different varieties, from the small sand shark to the large black tipped shark from southern waters.

In handling the skins the regular beamhouse methods of liming were first attempted. It was found, however, that the skins disintegrated to such an extent that this method could not be used. Many other tests were made, but the one that finally gave the best results consisted of the following treatment: Upon arrival the skins were cut into sides, in order to overcome the difficulty encountered in handling the whole skins, due to the two fin holes in the middle of the body. The sides were soaked for twenty-four hours and then washed thoroughly. The washed skins were next transferred to a two-tenths of 1 per cent. solution of caustic soda in a paddle, where they were allowed to remain for two days with occasional stirring. After treatment with caustic soda the skins were washed well and fleshed on a machine or by hand. The grain side, still very harsh, was beamed by hand with a blunt knife to remove as much of the shagreen as possible. Great difficulty has been encountered in removing the outer layer, which in appearance is very much like a rough sandpaper. By the caustic soda treatment, however, it can be partly eliminated and the stock rendered suitable for certain grades of leather.

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The fleshed and beamed stock was next bated with ammonium chloride, using 3 per cent. on the weight of the stock at a temperature of 100° F. Following bating, the skins were washed and were then ready for the actual tanning operation.

Several methods of tanning were employed, but the one giving the best results was as follows: The bated skins were placed in a drum with a solution containing 5 per cent. of sodium dichromate and 2½ per cent. of sulphuric acid with 5 gallons of water to each 100 pounds of stock. When thoroughly penetrated the skins are horsed up overnight in order to allow the chrome to set. The following day the skins are returned to the drum and treated with a solution of 6 pounds of sodium bisulphite, using 4 gallons of solution to each 100 pounds of stock. The skins are run in the solution until the chrome is entirely reduced and then horsed up again overnight to complete dehydration.

If desired, the skins, after the above chrome tanning, can be finished, as is common practice for chrome tanned stock. Better results, however, are obtained by giving the stock a retan as follows: The chrome tanned stock is set out, shaved on the flesh, washed slightly and then run in a solution of quebracho extract at 10° Bk. for one hour. The strength of the liquor is then increased to 30° Bk. and the stock run in this stronger liquor until struck through. When well struck through, the skins are put in a layer for five days, containing a 40° Bk. quebracho extract liquor.

The tanned skins may be either fat-liquored or stuffed, according to the grade of leather desired. If it is to be finished on the grain, the stock is washed and colored as desired, and then fat-liquored with a heavy fat liquor, using soluble oil as the carrying agent. The fat-liquored skins are then dried out, sammied back, staked, tacked, and finished. The final finish should be of a nature that will lend itself to brushing.

Very good results were obtained by hand buffing the flesh and applying a cordovan finish. In doing this, however, it is necessary to stuff the leather rather than fat-liquor it. The stuffing which gave the best results consisted of a mixture of 3 pounds of tallow and 7 pounds of cod oil on each 100 pounds wet weight; and was finally driven in with 3 pounds of sulphonated cod oil in a small quantity of warm water. On drying out the leather

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should be sammied, staked, and hand buffed. The buffed leather is then colored by hand and a cordovan finish applied.

Wearing tests were made on shoes made from shark skins and showed exceptional durability.

MODERN THEORIES OF THE VARIOUS METHODS OF TANNING.

By Professor Louis Meunier.

[Translated from *Chimie et Industrie*, 1, 71-80 and 272-276 (1918).]

Knapp[1] was the first chemist to undertake scientific study of the theory of tanning. He regarded leather as composed of hide substance in which the fibers had become imputrescible by dehydration and were completely separated from one another. This definition therefore applied to the product which he obtained by dehydrating hide substance with alcohol. It applies equally well to the product that we obtained[2] by producing dehydration by means of saturated solutions of potassium carbonate or sodium thiosulphate. In both cases a white product is obtained which exhibits, upon cutting, completely separated fibers having quite the outer appearance of leather. Unfortunately, when placed in water, it swells, regaining its normal proportion of water and its general condition prior to tanning; it once more becomes putrescible, convertible into gelatin by boiling water, and, if dried again, the fibers become glued together yielding a horny mass. Knapp's definition is therefore much too broad.

On the other hand, it would be extreme to regard as making leather only those substances which render the fibers completely insoluble and resistant to the action of boiling water because tawed leathers, those tanned with alum, would then not be included in the definition.

Let us rather consider leather as an imputrescible modification of skin tissue in which the dehydrated fibers are separated from each other and exhibit a more or less marked resistance to the action of both cold and boiling water. As the intensity of a

[1] *Dingler's Polytechnisches Journal*, **149**, 305.

[2] Meunier and Seyewetz, *Collegium*, 1912, p. 54; this JOURNAL, 7, 230 (1912).

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tannage is greater, so will the resistance to boiling water be greater; in fact, upon this principle, Fahrion[3] has devised a method for determining tanning values.

Composition of Skin Ready for Tanning.

In preparing a skin for any of the various tannages, all of the component parts are removed excepting the derma, or true skin, and the hyaline layer which covers the derma.

The Hyaline Layer.—The chemical composition of this layer has been little studied; it is known, nevertheless, that the protein matter composing it fixes tannins more rapidly than that of the derma. It resists the action of digestive ferments and is but little affected by dilute acids and alkalies. It constitutes the *grain* of the tanned skin.

The Derma.—This layer is made up of white fibers, or connective tissue, composed of collagen, a protein which is converted into gelatin by boiling water and is decomposed by pepsin in acid solution, but which is very little acted upon by trypsin in neutral or slightly alkaline solution. Between the fibers, in colloidal solution, is what is known as coriin and which appears to be an albumose derived from the partial hydrolysis of the collagen. Collagen is amphoteric, has a high molecular weight, probably greater than 3,000, and contains both amino and carboxyl groups, the amino groups predominating to such an extent as to make hide substance primarily basic in action. These amino groups are the sensitive points of the molecule and the ones which are attacked by putrefactive bacteria, by digestive ferments, by boiling water, and by most tanning materials. These basic groups likewise make the skin capable of combining vigorously with dilute acids, forming true salts. It is not yet known, however, whether these amino groups are primary, secondary, or tertiary.

In considering hide substance as a condensation product of amino acids, formed thus:

$$n(NH_2.R.COOH) \rightleftharpoons NH_2.R.CO.NH.R.CO. - - - .NH.R.COOH + (n - 1)H_2O,$$

we should evidently have to have at least one terminal amino group. But it is possible to produce a salt by closing the chain,

[3] *Chemiker Zeitung*, 1908, p. 888; this JOURNAL, 4, 60 (1909).

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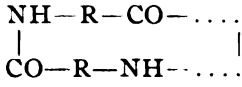
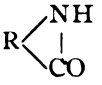


Now it is known[4] that pepsin attacks proteins with closed-ring structures while trypsin hydrolyzes chains of amino acids with terminal amino groups. Since pepsin decomposes connective tissue while trypsin is almost without action upon it, the closed-ring structure for collagen is the more probable.

Stiasny,[5] from a study of the diazotizing of skin, concludes that there are no primary amino groups present, as in

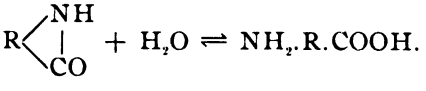


Stiasny's experiments and conclusions are contested by Fahrion,[6] who, without definite proof, believes in the existence of at least one primary amino group in the hide molecule. The affinity of hide substance for dilute acids and the activity of its reactions with formaldehyde and quinone contend, as we shall see further on, in favor of Fahrion's hypothesis.

Gelatin.—This protein appears to be a product of depolymerization, and perhaps of hydration, of hide substance. Since gelatin is attacked by trypsin, it would seem that the open-chain structure

$$NH_2.R.COOH$$

can be applied to it and we should then have, admitting the hypothesis of hydration,



In the pure state, the percentage composition of gelatin, according to Sadikoff, is as follows:

Carbon	50.90
Hydrogen	6.80
Oxygen	23.80
Nitrogen	17.97
Sulphur	0.53

[4] J. A. Wilson, this JOURNAL, **12**, 108 (1918).
[5] *Collegium*, 1908, p. 117; this JOURNAL, **3**, 246 (1908).
[6] Moniteur scientifique du Dr. Quesneville, 1911, p. 373.

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Among the more abundant products of hydrolysis of gelatin are the following:

$$\text{Glycocoll, } NH_2.CH.COOH$$

$$\text{Glutamic acid, } \begin{array}{l} HOOC.CH_2.CH_2.CH.COOH \\ \qquad\qquad\qquad\quad\;\; | \\ \qquad\qquad\qquad\quad NH_2 \end{array}$$

and the hexone bases, Arginine,

$$\begin{array}{l} HN \diagdown \\ \qquad\; C.NH.CH_2.CH_2.CH_2.CH.COOH \\ H_2N \diagup \qquad\qquad\qquad\qquad\quad\;\; | \\ \qquad\qquad\qquad\qquad\qquad\quad\; NH_2 \end{array}$$

and Lysine,

$$\begin{array}{l} H_2N.CH_2.CH_2.CH_2.CH_2.CH.COOH \\ \qquad\qquad\qquad\qquad\quad\;\; | \\ \qquad\qquad\qquad\qquad\quad NH_2 \end{array}$$

All these bodies conform to the general formula

$$\begin{array}{l} R.CH.COOH \\ \quad\; | \\ \quad NH_2 \end{array}$$

Having seen the relation between hide substance and gelatin and the greater ease of experimenting with gelatin, one finds it advantageous to study the effect of new tanning materials upon the solubility of gelatin before applying them to actual tanning.

TANNING WITH VEGETABLE TANNING MATERIALS.

Vegetable Tannins.—The question of the constitution of vegetable tanning materials has hardly been even outlined. The only tannins about whose constitution definite information can be given are gallotannic and ellagitannic acids. The recent work of Fischer and Freudenberg[7] has shown that gallotannic acid generally exists in vegetable matters in the form of a glucoside to which they attribute the formula

$$\begin{array}{l} \ulcorner\text{———————O———————}\urcorner \\ | \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CHOR—CHOR—CHOR—CH—CHOR—CH_2OR \end{array}$$

in which R represents the group,

$$(OH)_3C_6H_2 — COO — C_6H_2(OH)_2CO.$$

[7] Berichte der deutschen chemischen Gesellschaft, 1912, p. 915, and 1913, p. 3253; this JOURNAL, 7, 390 (1912).

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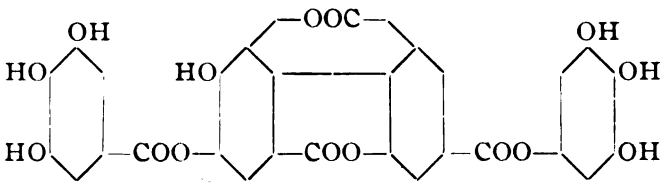
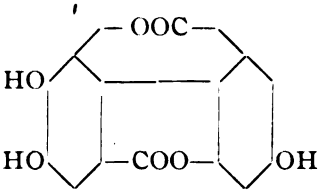
For ellagitannic acid, Perkin and Nierenstein[8] have proposed the formula



From the standpoint of general character and tanning properties, the vegetable tannins are divided into two very distinct classes, the *pyrogallol* tannins and the *catechol* tannins, which can, moreover, exist together in the same material. The tannins of chestnut wood, oak, myrobalans, sumac, valonia, etc., are pyrogallol tannins and when subjected to dry distillation they yield pyrogallol. When hydrolyzed by dilute acids, they give, besides glucose, gallic acid or a mixture of gallic and ellagic acids. To ellagic acid is generally given the formula[9]



The tannins of quebracho, mangrove, mimosa, and hemlock are catechol tannins. When subjected to dry distillation, they give off pyrocatechin and when heated with dilute acids, they yield neither gallic nor ellagic acids, but some insoluble red matter of unknown constitution, but designated by the name *phlobaphenes.*

Phlobaphenes, according to Etti,[10] should be considered as anhydrides of catechol tannins, whose solubilities decrease as they become less hydrated. Korner considers them as oxidation products of the tannins, which hypothesis appears the more likely.

The analytic separation of pyrogallol from catechol tannins is effected by the formaldehyde-hydrochloric acid reaction. A convenient quantity of solution is heated with a mixture of formaldehyde and HCl whereupon all the catechol tannins combine with

[8] *Trans. Chem. Soc.*, **87**, 1428 (1905).

[9] *Ber. deutsch. chem. Ges.*, 1903, p. 212, and *Collegium*, 1905, p. 382.

[10] *Monatshefte für Chemie*, **1**, 262, and **4**, 512.

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formaldehyde forming insoluble compounds. It is now only necessary to filter and test for pyrogallol tannins in the filtrate with iron alum, after addition of an excess of sodium acetate.

Moeller has promulgated a rather original theory of the relation existing between tannins and phlobaphenes. His view[11] is that all vegetable tannins contain two distinct substances: the one a soluble, crystalloidal "peptizer," usually called tannin, or tannic acid; the other, an insoluble "peptizable" gel, composed of ellagic acid, the catechins, and the phlobaphenes. Of these substances, ellagic acid and the catechins are monomolecular, while the phlobaphenes are polymerized. The pyrogallol tannins contain some peptizing tannin, some ellagic acid, and their phlobaphenes. The catechol tannins contain a small quantity of peptizing tannin and are composed almost exclusively of catechins and their polymers, the catechol phlobaphenes. The variation in character of aqueous solutions of tanning extracts depends, according to Moeller, upon the relative proportions of peptizing and peptizable substances in the vegetable material extracted, provided that at the time of extraction the peptizing matter exerts a solvent action upon the peptizable substances. The "peptization" will evidently be less marked in extractions made in the cold than in those carried on at high temperatures, other things being equal.

The Mechanism of Tanning.—Having recalled these few generalities regarding tanning materials, let us now examine the phenomena which result when hide substance is brought into contact with tan liquors. At the moment of contact, the fibers are composed of a kind of albuminoid gel swollen by water. The tan liquors, on the other hand, consist of sols of emulsoid colloids; in these solutions the tannins act as true colloids, since they do not lower the freezing point of water.

The works of Fahrion,[12] of Stiasny,[13] and of Meunier and Seyewetz[14] permit the regarding of vegetable tanning as consisting of two distinct series of phenomena: those of a chemical nature, made clear by the researches of Fahrion, on the one hand,

[11] *Collegium* (London edition), 1917, p. 38.

[12] *Monit. Scient.*, 1911, p. 361, and 1914, p. 112.

[13] *Chemiker Zeitung*, 1907, p. 1270, and *Collegium*, 1908, p. 117; this JOURNAL, 3, 246 (1908).

[14] *Collegium*, 1908, p. 195, and *Monit. Scient.*, 1909, p. 91.

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and of Meunier and Seyewetz on the other; and those of absorption and irreversible transformation, brought out by Stiasny's researches.

Phenomena of Exclusively Chemical Nature.—We have recalled the results acquired upon the chemical constitution of the tannins and may conclude that the tannins are naturally classed under the heading of phenols with acid functions. Meunier and Seyewetz have studied the general properties of phenols as tanning agents, or, more exactly, as agents for rendering gelatin and hide fiber insoluble. They demonstrated very clearly that aqueous solutions of pure phenols produce only an extremely feeble effect upon the solubility of gelatin, but their oxidation products quickly render gelatin insoluble. In the accompanying table are listed the results of a number of experiments in which gelatin plates weighing 4 grams were placed in 250 cc. of 1 per cent. solutions of various phenols to which had been added 30 cc. of 25 per cent. sodium carbonate solution.

Reagents	Action of boiling water upon gelatin.	
	Experiments carried out in contact with air. Rendered insoluble after	Experiments carried out not in contact with air. Rendered soluble after
Gallic acid	3 days	44 days
α-Naphthol	14 days	44 days
β-Naphthol	7 days	44 days
Hydroquinone	35 hours	44 days
Pyrogallol	35 hours	44 days
Diaminophenol, hydrochloride	23 days	44 days
Resorcinol	37 days	44 days

From these results it is convenient to select the two which behave similarly, hydroquinone and pyrogallol, because of the speed with which they rendered gelatin insoluble when acting in contact with air and in alkaline solution, conditions favorable to their oxidation. We have particularly examined the properties of hydroquinone because of the ease of preparing in the pure state its oxidation product, benzoquinone.

There was evidently cause for anticipating that this oxidation product, employed directly, would possess very marked power of rendering gelatin insoluble. Indeed, experiment has shown that if 20 grams of thin gelatin plates be first swollen in water and then immersed in a liter of 4 per cent. quinone solution, at 15°

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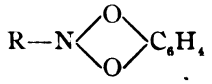
for 1¾ hours, the gelatin will have become completely insoluble in boiling water. It is then of a reddish-brown color, like the gelatin made insoluble by hydroquinone in contact with air and alkali. Hide fiber, too, is rendered insoluble in boiling water by the action of quinone, exactly as in the case of gelatin. If bated skin, which is neutral, or better, slightly acid with an organic acid like acetic or butyric, be subjected to the progressive action of quinone, using about 1.5 parts of quinone per 100 of pelt, the color of the skin will be seen to change successively to light rose, to violet, and then to brown. When the operation is complete, the skin will resist the action of boiling water, will be insoluble and will have been transformed into a leather of remarkable resistance.

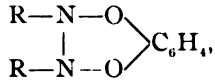
The reaction between the quinone and protein matter is a truly chemical action, which is accompanied by the reduction of a part of the quinone to hydroquinone. This latter substance is easily detected by extracting from the residual quinone liquor with ether, after tanning. During the tannage part of the quinone has oxidized the hide fibers, being itself reduced to hydroquinone. The oxidized fibers then combine with the quinone left in solution. The action is similar to that of quinone upon aromatic amines:

$$C_6H_5NH_2 + 2C_6H_4O_2 = C_6H_5N(C_6H_4O_2) + C_6H_4(OH)_2$$

$$2C_6H_5NH_2 + 3C_6H_4O_2 = (C_6H_5N)_2C_6H_4O_2 + 2C_6H_4(OH)_2.$$

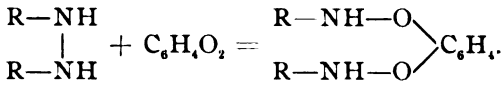
It is therefore probable in the case of hide fiber also that there are amino groups present which undergo oxidation. If we admit the existence of primary amino groups in the protein molecule, the compounds formed might be represented by the formulas:





Fahrion (*loc. cit.*) admits the following reactions:

$$2RNH_2 + O = R{-}NH{-}NH{-}R + H_2O$$



In consequence of the foregoing, it seems logical to admit that among the polyphenols composing vegetable tanning materials, certain of them are capable of furnishing by oxidation quinones

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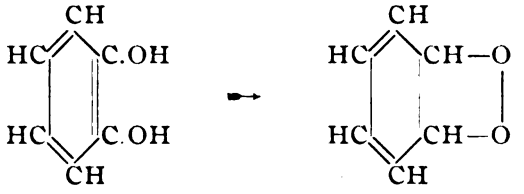
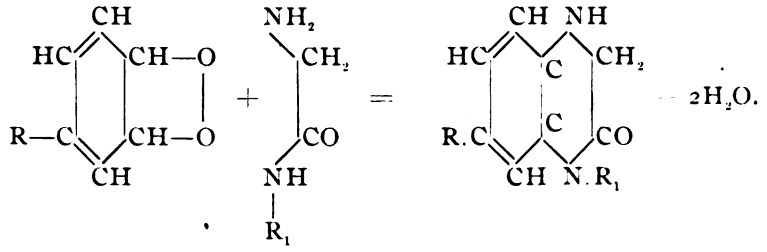
reacting chemically with protein matter, following the mechanism which we have just indicated for benzoquinone; *i. e.*, some of the quinones oxidize the amino groups of the protein molecules, which then combine with the quinones remaining in solution. This conclusion is much the same as that of Fahrion.

Powarnin[15] does not accept the hypothesis of the formation of quinones by oxidation in the tan liquors, but holds that in tanning materials themselves the phenolic bodies undergo isomeric change forming quinones without the introduction of oxygen from an outside source. For example, the following would represent the change in the case of pyrocatechin:



A tannin possessing, say, two hydroxy groups in ortho positions would react with protein matter following the mechanism:



We mentioned above that the weight of quinone necessary to render hide fiber insoluble is very small compared with the weight of hide fiber and is also very small compared with the total weight of tannin found in leather, which is, on an average, half of the weight of the leather. One may therefore anticipate that some other phenomenon governing the fixation of large quantities of tannins plays a part in the formation of leather.

Adsorption Phenomena and Irreversible Transformation.—We have said that solutions of vegetable tannins could be considered true colloidal solutions. The colloidal character of these solu-

[15] *Collegium*, 1914, p. 634; this JOURNAL, **9**, 567 (1914).

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tions is demonstrated by their lack of influence upon the freezing point of water, by their precipitation by means of colloids of opposite sign, as albumin, gelatin, gum arabic, etc., by their slight power of diffusion and feeble osmotic pressures, by the opalescence of tan liquors, etc. Paterno[16] announced in 1889 that the molecular weight of tannin in acetic acid solution was normal, which seemed to indicate that solutions of tannin in acetic acid were true solutions. He recognized later,[17] however, that his cryoscopic determinations had been thrown out by the presence of impurities and he concluded that, after all, tannin dissolved in acetic acid is in the colloidal state, just as it is in water.

The Swelling of Skin Tissue.—Let us now examine the condition of the hide substance at the instant it comes into contact with the tannins. If a rapid tannage is to be employed, the hides are subjected to an operation which replaces the alkaline reaction which they possessed after unhairing by a slightly acid one. If a slow tannage is used, the first liquors employed, which are made by exhausting used bark, contain insignificant amounts of tannin, but large quantities of organic acids which give the hides an acid reaction before they come into contact with appreciable amounts of tannin.

The changes which hide substance undergoes in contact with dilute acids have been brought to light by the work of Procter.[18] In his researches Procter likewise substituted gelatin for hide substance. If gelatin be immersed in acid solution, it will swell to a much greater extent than in pure water; for example, a gelatin which swells to eight times its volume in pure water may absorb as much as fifty times its volume of water in a very dilute hydrochloric acid solution. In other words, gelatin hydrochloride, obtained by saturating the basic amino groups with hydrochloric acid, has a much greater power of absorbing water than gelatin itself.

If gelatin be placed in pure water and a highly ionized acid, like hydrochloric, be added in successive portions, time being

[16] *Zeitschrift für physikalische Chemie*, 1889, p. 457.

[17] *Kolloid Zeitschrift*, 1913, p. 81.

[18] *Kolloidchemische Beihefte*, 1911, p. 243; this JOURNAL, **6**, 270 (1911).
Trans. Chem. Soc., **105**, 313 (1914); this JOURNAL, **9**, 207 (1914).
Ibid., **109**, 307 (1916); this JOURNAL, **11**, 261 (1916).
Ibid., **109**, 1327 (1916); this JOURNAL, **12**, 76 (1917).

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allowed after each addition for the establishment of equilibrium, it will be found that the swelling of the gelatin increases very rapidly at first, but reaches a maximum (for 0.6 gram HCl per liter) and then diminishes continuously as the concentration of acid is increased. If this series of experiments be repeated, using a weak acid like acetic or lactic, the swelling will increase steadily with the concentration until the solution becomes so strongly acid as to dissolve the gelatin.

Hide substance behaves much like gelatin and it can be said that a skin subjected to the action of dilute acids, before tanning, has undergone marked swelling, which tends to give it the character of a homogeneous hydrogel, in which the fibrillary structure has largely disappeared. The disappearance of this structure is only partial and in every case it reappears as soon as tanning has begun, especially under the action of quinones, which react chemically.

Adsorption of Tannin by Skin Tissue.—In the light of what has just been explained concerning the nature of tan liquors and hide substance ready for tanning, we are first of all led to examine the action of a gel upon a colloidal solution. When a gel is placed in a colloidal solution, there takes place a very marked adsorption or pseudo-adsorption, according as the phenomenon is reversible or irreversible. If a silica gel be added to a solution of fuchsin, the latter is adsorbed by the gel, but is not removed again even by prolonged washing with water; such adsorption is irreversible and should be considered rather as a pseudo-adsorption.

The penetration of different tannins into gelatin has been studied by Hoppenstedt[19] who showed that the diffusion of pyrogallol tannins into the gels was very marked while that of catechol tannins was only slight.

According to Procter and Wilson[20] the fixation of tannin by the hide fiber is the result of an electrical neutralization which can be explained by the existence of negative electrical potentials on the colloidal particles of tannin and of positive potentials on the protein matter in the presence of an acid.

In the case of tannin reversibly adsorbed by hide substance,

[19] This JOURNAL, **6**, 343 (1911).

[20] *Trans. Chem. Soc.*, **109**, 1327 (1916); this JOURNAL, **12**, 76 (1917).

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there appears to be a gradual, although only partial, transformation to the irreversible form. In fact, it is known that vegetable tanned leather contains more soluble tannins immediately after tanning than after storing for a time; there is a partial transformation of the tannin adsorbed from the reversible to the irreversible form. It is very probable that this transformation is influenced by secondary phenomena of a chemical nature, such as oxidation, dehydration and polymerization. The insoluble, irreversible tannin seems to have a constitution identical with that of the phlobaphenes described above. It is also possible that the transformation results from a deeper penetration of the adsorbed tannin into the interior of the fibers. When tanning has progressed to the point where the fibrillary structure of the hide again appears, it is necessary to consider, not only the tannin precipitated within each fiber functioning as a gel, but also the tannin concentrated upon the surface of the fiber, according to Gibbs' law. It is only natural to suppose that the tannin gel concentrated at the surface of the fibers slowly and steadily penetrates into the mass of each fiber, and it is very evident that tannin which has penetrated the fibers will be more difficult to remove by washing than that at the surface. Accompanying the adsorption there is a progressive dehydration of the hide gel, which is the cause of the hide regaining its fibrous structure as tanning progresses, and the liquor within the gel becomes more concentrated. This dehydration is therefore the consequence of osmotic phenomena.

Application.—The preceding considerations furnish interesting information regarding the method of tanning applied to any given leather. Added to results obtained from other sources, they make it possible for a trained specialist to reason out how the leather was tanned. For example, take sole leather, which can be obtained in French manufacture tanned exclusively by weak oak bark liquors (slow tannage), tanned with medium strength liquors of bark and concentrated extracts (mixed tannage), and tanned with strong liquors prepared entirely from concentrated extracts (rapid tannage). In the case of slow tannage, it is evident that chemical action and the transformation of adsorbed tannin to the irreversible, insoluble form are maxima and the leather resists the prolonged action of water; when 5 grams of

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leather shavings are shaken with 250 cc. of water for five hours, the extracted matter, when dried, never exceeds 14 per cent. of the weight of absolutely dry leather. In the case of rapid tannages, chemical action and the transformation of adsorbed tannins are very much less marked and the content of water soluble matter is greater, reaching, in some cases, as much as 30 per cent. of the weight of absolutely dry leather.

It is easy to understand also that, other things being the same, the quality of a leather depends upon the nature of the tanning materials used in its manufacture. Their richness in quinones and quinonizable substances, the sensitivity of the solutions to adsorption phenomena, the ease with which the adsorbed tannins assume the irreversible form are all factors which vary with different tanning materials. There is little in common between a leather tanned with oak nut-galls and one tanned with untreated quebracho; the first is not very resistant to the action of water, the second very much so. Tanning materials rich in phlobaphenes will give leathers with low water-soluble contents; the tannin of oak nut-galls does not yield phlobaphenes, while quebracho contains large proportions.

Conclusions.—The tanning of skin tissue by vegetable tanning materials can be considered as the result of the following phenomena proceeding simultaneously:

1. Chemical reaction with the products of quinone structure existing in the tan liquors.

2. Adsorption, or pseudo-adsorption, causing the precipitation of colloidal tannin, either by the action of the gel constituting the swollen hide fiber, or by means of the concentrating of the solution at the surface of the fibers, following Gibbs' law.

3. Transformation of a part of the precipitated tannin from the reversible to the irreversible, insoluble form, together with chemical reactions (oxidation, hydration, or polymerization) and deeper penetration of the concentrated tannin gel into the hide gel.

4. Osmotic phenomena causing dehydration of the swollen hide fiber and increasingly marked formation of a fibrillary structure.

Note.—We should point out in closing that the use of the electric current for accelerating tanning has been studied by Wil-

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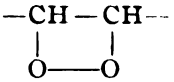
liams[21] and by Rideal and Evens.[22] Their work has shown that some tannin in the liquors is destroyed by direct, but not by alternating currents, but it is possible to accelerate the tanning action by cataphoresis.

Tanning with Fish Oils.

It is well known that this method of tanning is designated by the name chamoising and consists in impregnating the suitably prepared skin with fish oils (cod oil, Japan fish oil) or the oil of marine animals (whale, seal, etc.). The penetration of the oils into the interior of the skin is brought about by energetic milling, which is interrupted from time to time to expose the skins to air in a condition favorable to the oxidation of the oils. They are watched closely during this exposure to air to prevent the heat which is developed from causing too high a temperature. As tanning proceeds, the skin loses its water and assumes a yellow color and a fibrous structure. When the tannage is complete, the excess of oily matter is pressed out and furnishes an emulsion which contains about 15 per cent. of water and is called *moellon*. The manufacture is completed by washing the leather with dilute sodium carbonate solution, which removes most of the oil or free fatty acids remaining.

A very complete study of the theory of tanning with fish oils has been made by Fahrion,[23] according to whom the active agents in chamoising are the unsaturated free fatty acids in the fish oils. According to Heyerdall,[24] these fatty acids correspond to formula $C_{17}H_{26}O_2$ and according to Tsujimoto[25] to the formula $C_{18}H_{28}O_2$. These acids possess four double bonds of which two are capable of oxidation by the air giving a peroxide structure,



resembling the peroxide structure attributed to quinone

[21] *Collegium*, 1913, p. 76; this JOURNAL, 8, 328 (1913).

[22] *J. S. C. I.*, 32, 633 (1913); this JOURNAL, 8, 331 (1913).

[23] *Zeitschrift für angewandte Chemie*, 1903, p. 665, and 1911, p. 2083; *Monit. Scient.*, 1904, p. 112, and 1911, p. 361.

[24] *Chemiker Zeitung*, 1896, p. 375.

[25] *Journal College Engineering*, Tokio, 1908, p. 193.

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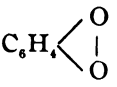
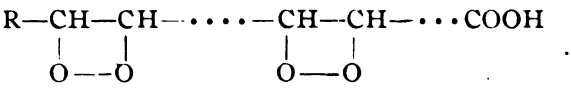
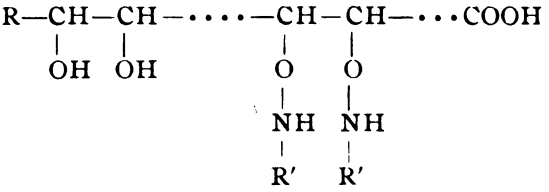


The peroxide acids can therefore be represented by the formula



(1)

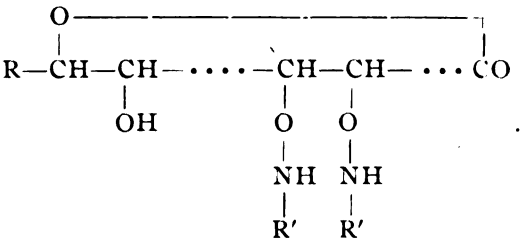
If we adopt the reduced formula $R'NH_2$ for the protein molecule, the reactions which come into play yield, according to Fahrion, the complex



(2)

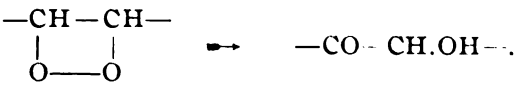
following a mechanism similar to that which we have established in the case of quinone.

Finally a lactonization is produced between the carboxyl group and the more distant hydroxy group,



(3)

Only a portion of the peroxide acids of formula (1) enter into combination with the protein matter, the rest being converted by molecular rearrangement into hydroxy acids,



These hydroxy acids are then capable of becoming lactonized, furnishing bodies no longer titratable in the cold by alkaline solutions (disguised fatty acids) and which are retained mechanically,

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in a feeble way, by the skin. These lactones are evidently saponifiable by alkalies upon the application of heat. In every case, there is really only a small part of the oxygen absorbed by the acids which intervenes in true tanning giving rise to complexes (2) and (3).

In order that a fatty acid be capable of chamoising, according to the mechanism described above, it must be unsaturated, having more than one double bond. Thus if a skin, previously dehydrated with alcohol, be tanned, as for ordinary chamois, with an alcoholic solution of oleic acid, a soft leather is obtained; but after draining off the alcohol to remove excess of oleic acid, the skin does not show any sign of being tanned when placed in water.

Let us now replace the oleic acid by the fatty acids of colza oil, which belong to the series $C_nH_{2n-4}O_2$ with two double bonds and which also include a little linolenic acid, $C_{18}H_{30}O_2$, with three double bonds. Operating as with oleic acid, one obtains a yellow leather much more resistant to the action of water. The leathers known as "Japanese," much appreciated for certain uses, are obtained by working the skin with colza oil with active intervention of oxygen from the air.

Finally, if we substitute linseed oil, rich in linoleic acid, for colza oil, the resistance of the resulting leather to water is still further improved, but is inferior to that of leather prepared under the same conditions with the fatty acids of cod liver oil, which belong to the series $C_nH_{2n-8}O_2$ and contain four double bonds in their molecules.

To sum up, tannage by fish oils results from the presence in these oils of free fatty acids possessing four double bonds, of which at least two are capable of saturation by absorption of oxygen giving bi-peroxides.

1. Part of the bi-peroxide acids react chemically with the protein matter, like quinone; one of the peroxide groups attacks the amino groups, which are oxidized by loss of hydrogen; the hydrogen thus liberated transforms the oxygen of the second peroxide group into two hydroxy groups; finally one of the hydroxy groups thus formed lactonizes the carboxyl of the fatty acid.

2. Another portion of the peroxide acids undergoes molecular rearrangement, causing the appearance of hydroxy groups which

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form lactones with the carboxyl groups. These lactones or "disguised fatty acids" are retained by the fibers, probably because they are insensitive to the alkaline washing which completes the manufacture of chamois leather.

Tanning with Formaldehyde.

The use of formaldehyde in tanning was patented by Payne and Pullmann[26] in 1898. According to these authors the action of formaldehyde gives practical results only in the presence of weak alkalies, particularly sodium and potassium carbonates. I have shown[27] that in preparing a leather by using simultaneously alkali carbonate and formaldehyde, two independent actions are discernible:

1. Osmotic dehydration produced by the salt solution and bringing about the separation of the fibers.

2. True tanning action caused by the formaldehyde, which fixes the separated fibers and renders them less sensitive to the action of water. I have shown, likewise, that the alkali carbonates can be replaced by other very soluble mineral salts, such as sodium thiosulphate.

It seems, at the moment, that the real tanning action of formaldehyde is brought about by attacking the nitrogen groups of the protein molecule,[28] following one of the two equations:

$$RNH_2 + HCOH \rightleftharpoons R - N = CH_2 + H_2O$$

$$2RNH_2 + HCOH \rightleftharpoons (R - NH -)_2CH_2 + H_2O.$$

Just as in quinone and fish-oil tannages, there is here, too, oxidation of the protein matter through reaction with the amino groups. The tanning properties of formaldehyde are not common to all aldehydes, for Fahrion has shown that a very scant tannage is obtained when benzaldehyde is substituted for formaldehyde.

Tanning with Alum.

Alum tannages are used in the manufacture of harness and of tawed leathers. In both cases salt is used in conjunction with alum.

[26] English patent No. 2872, Feb. 4, 1898.

[27] Meunier, *Collegium*, 1912, p. 420; this JOURNAL, 7, 574 (1912).

[28] Nierenstein, *Collegium*, 1905, p. 159, and Fahrion (loc. cit.).

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Action of Aluminum Sulphate Alone.—Let us examine the phenomena which manifest themselves when a skin is penetrated by a solution of pure aluminum sulphate. This salt hydrolyzes freely yielding sulphuric acid and a soluble basic aluminum sulphate, or a colloidal sol of alumina. We have seen that in spite of its amphoteric character, hide substance is rather basic. In consequence, the hide absorbs the sulphuric acid liberated from the aluminum sulphate by hydrolysis, thus disturbing the equilibrium and causing further hydrolysis until all of the basic groups are saturated. As for the alumina sol, it will be adsorbed, just like a tannin sol of the vegetable tannins:

1. by penetration into the gel composed of swollen hide fiber, in which it coagulates.
2. by coagulation upon the surface of the fibers, because of its greater concentration there.

If such a skin be dried, a hard and brittle leather is obtained, which is the result of two distinct facts:

1. the swelling of the fibers by sulphuric acid, which tends to eliminate the fibrous structure and give a homogeneous mass.
2. the absence of very marked adsorption of alumina; the adsorption is reversible and upon washing with water, the fibers lose the greater portion of the matter adsorbed.

However, the reversible phenomenon tends to become irreversible with time, because the alumina undergoes a slow modification and probably also because this alumina penetrates more deeply into the mass of each fiber. And finally, it is possible that in time there is formed a true chemical combination between the hide substance and the metallic oxide. According to Wilson[29] we should have

$$3R\begin{cases}NH\\ |\\ CO\end{cases} + Al(OH)_3 \rightleftharpoons (NH_2 - R - COO)_3Al.$$

In a work entirely upon the theory of alum tannage, Nihoul[30]

[29] This JOURNAL, **12**, 108 (1917).

[30] *Collegium* (London edition), 1916, p. 178; this JOURNAL, **12**, 36 (1917).

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has studied the possibilities of the chemical action of mineral salts upon the protein matter composing the skin substance.

Action of Aluminum Sulphate in the Presence of Salt.—From what precedes, it follows that to improve the tannage with aluminum sulphate, it is advisable to hinder the undue swelling of the skin by sulphuric acid and to increase as much as possible the amount of alumina adsorbed. This double problem can be solved in two different ways:

1. By using, instead of the normal salt, aluminum sulphate rendered basic by addition of alkali. In this case the swelling is less marked, the proportion of alumina adsorbed is greater, and the adsorption is reversible to a lesser extent than in the case of the normal salt.

2. By adding to the aluminum sulphate a certain quantity of common salt. The swelling is diminished by a mechanism similar to that occurring in pickling and the osmotic pressure forces water from the interior of the skin. On the other hand, the increase in concentration of electrolytes facilitates the flocculation of the alumina hydrogel and thus increases the proportion fixed by the skin. In other words, the presence of salt increases the tanning action and diminishes the undue swelling obtained with aluminum sulphate alone.

The chief difficulty with leather tanned with alum and salt lies in its poor resistance to the action of water. If such leather be washed with water, the salt in the interior of the skin is soon removed to such an extent that the skin, subjected only to the action of sulphuric acid, swells again excessively, while so much acid and alumina are removed as to lower considerably the degree of tannage and render the leather hard when dried. As we have said before, the resistance to water of leather tanned with alum and salt increases with time and the redissolving of the alumina hydrogel becomes more and more difficult.

Tanning with Chrome.

One-Bath Tannage.—The method of chrome tanning known as "one-bath" consists in subjecting the skin, suitably prepared, to the action of a basic solution of chromic salt, made either by adding alkali to a normal chromic salt or by reducing an alkali bichromate with glycerine, glucose, starch, etc., in the presence

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of the proper quantity of acid. Now it is known that in violet and green solutions of chromic salts there is more or less marked hydrolysis, the proportion of free sulphuric acid depending upon the dilution and temperature of the solution. Recoura[31] has demonstrated by thermo-chemical measurements that when a solution of violet chromic sulphate, $Cr_2O_3(SO_3)_3$, is heated, it dissociates into free sulphuric acid and green basic sulphate:

$$2Cr_2O_3(SO_3)_3 + H_2O \rightleftharpoons H_2SO_4 + (Cr_2O_3)_2(SO_3)_5.$$

The hydrolysis of basic salts is evidently less than that of normal salts, but nevertheless exists to some extent. These basic and uncrystallizable salts can, moreover, be considered as colloidal solutions of chromic oxide in the normal unhydrolyzed salt.

A skin placed in chrome liquor is therefore in contact with

1. free sulphuric acid,
2. unhydrolyzed chromic salt,
3. chromic oxide in colloidal solution in the unhydrolyzed salt.

The free sulphuric acid rapidly penetrates into the interior of the skin, where it becomes fixed, thus causing hydrolysis to continue until the establishment of a reversible equilibrium, which is rather quickly reached. The solution of chromic oxide in the normal salt penetrates more slowly because of its colloidal character. There is irreversible adsorption of chromic oxide, precipitation of a gel at the surface of the fibrils, and finally, slow and progressive penetration of this gel into the substance of the fibrils.

Because of the difference in speed of penetration of the sulphuric acid and chromic oxide, it is obvious that at the beginning of the tannage the liquor surrounding the skins becomes more basic, and that later this basicity steadily diminishes. Conversely, the solution within the fibers contains at the beginning an acid salt, which steadily becomes more basic.

The question which confronts us at once is whether or not the chromic oxide forms a true compound with the fibers. The recent researches of Davison[32] seem to show that there is only a simple adsorption phenomenon. Davison subjected equal weights

[31] *Revue Scientifique*, July, 1886.

[32] *J. Phys. Chem.*, 1917, p. 190; this JOURNAL, **12**, 258 (1917).

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of hide powder to a tannage in which the concentration of chromic salt was the only variable. When equilibrium was established, he determined the amount of chromic oxide in the liquid phase surrounding the hide powder and in the solid phase composed of the hide powder itself. By plotting the results in the form of a curve of which the abscissas represented the values of chromic oxide in the liquid phase and the ordinates these values in the solid phase, a curve was obtained in which no breaks, horizontal or vertical positions appeared. The phase rule indicates that we have an adsorption isotherm and that no chemical combination between hide powder and tanning material have been formed.

According to Wilson (*loc. cit.*) it is possible that in time a chemical combination is formed between the protein matter and the adsorbed oxide according to the equation:

$$3R\begin{matrix}NH\\|\\CO\end{matrix} + Cr(OH)_3 \rightleftharpoons (NH_2 - R - COO)_3Cr.$$

Two-Bath Tannage.—The two-bath method of chrome tanning consists of two separate operations:

1. The prepared skin is worked in a solution of sodium or potassium dichromate made acid with hydrochloric in order to liberate partially the chromic acid.

2. The skin is taken from the first bath and subjected to the action of a reducing liquor, generally consisting of a solution of sodium thiosulphate to which has been added hydrochloric acid.

Let us first of all examine what transpires in the first bath. There is no doubt that chromic acid is fixed by the basic groups of the protein molecule and the skin becomes colored yellow throughout. The formation of a salt by combination of the skin with chromic acid is unquestionable. Indeed Fahrion (*loc. cit.*) has shown that if samples of 1 gram of filter paper, cotton, silk, wool, or hide powder be treated with 25 cc. of water and 10 cc. of a ½ per cent. solution of chromic acid, the quantities of chromic acid fixed are

Filter paper	1.5 milligrams
Cotton	2.2 milligrams
Silk	14.2 milligrams
Wool	33.0 milligrams
Hide powder	33.3 milligrams

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The salt compound thus formed is not very stable and does not give a tannage, for it is decomposed by the action of boiling water which gelatinizes the collagen. It is known, however, that by prolonged action of light the phenomenon of auto-reduction takes place with the production of chromic oxide and the appearance of tanning. But in modern practice the skins coming from the first bath are left for only twelve hours at most before throwing into the second bath and so this auto-reduction is never very marked. In every case, the slight oxidation of the hide-substance acts upon the amino groups.

The first bath contains an excess of dichromate along with hydrochloric acid; the salt represses the ionization of the chromic acid in consequence of which the speed of fixation of the acid is diminished and the action made more regular.

The reactions taking place in the second bath, particularly when this is made up of sodium thiosulphate and hydrochloric acid, are very complex. They depend, besides, upon the method of adding the acid. The relative proportions of thiosulphate and acid used are about 12 kilograms of sodium thiosulphate and 6 kilograms of commercial hydrochloric acid for 100 kilograms of pelt, the acid being added slowly as the reduction progresses.

Under these conditions, according to Procter, the following procedure takes place. The skins, saturated with chromic acid, when put into the second bath, first of all take on a brown color arising from the formation of a basic chromic chromate according to the equation:

$$3CrO_3 + 6HCl + 6Na_2S_2O_3 \rightleftharpoons 3Na_2S_4O_6 + 6NaCl + H_2O + Cr_2(OH)_4CrO_4.$$

As the reaction proceeds, the color of the skins becomes brighter and the basic chromate is transformed into chromic chloride and the total reaction can be summed up in the equation:

$$2CrO_3 + 12HCl + 6Na_2S_2O_3 \rightleftharpoons 3Na_2S_4O_6 + 6H_2O + 6NaCl + Cr_2Cl_6.$$

At the same time the thiosulphate is decomposed with liberation of sulphur:

$$2CrO_3 + 6HCl + 3Na_2S_2O_3 \rightleftharpoons 3Na_2SO_4 + 3S + 3H_2O + Cr_2Cl_6.$$

When all the free hydrochloric acid has been used up, the excess

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of thiosulphate reacts with the normal chromic chloride giving a basic salt:

$$Cr_2Cl_6 + Na_2S_2O_3 + H_2O \rightleftharpoons Cr_2Cl_4(OH)_2 + SO_2 + S + 2NaCl$$

or

$$Cr_2Cl_6 + 2Na_2S_2O_3 + 2H_2O \rightleftharpoons Cr_2Cl_2(OH)_4 + 2SO_2 + 2S + 4NaCl.$$

The basic chromic salts thus formed in the interior of the skin react as we have noted for one-bath tannage. The essential difference between one-bath and two-bath tannages lies in the precipitation of a rather large proportion of sulphur in the skin by the latter process.

We have said that the skin upon coming from the first bath is saturated with chromic acid solution in consequence of the unstable and reversible combination. It follows that, if the skin upon coming from the first bath were plunged immediately into the second bath, a part of the chromic acid would diffuse out of the skin and become reduced in the bath itself and not in the interior of the fibers, which would be a defect in the process. To obviate this difficulty, the process is conducted in the following manner:

1. By keeping the skins, after coming from the first bath, for twelve hours before throwing them into the second bath, in such a manner as to favor a mild auto-reduction at the expense of the hide substance.

2. By fixing the surface chromic acid by plunging the skins for only a few seconds into a strong solution of sodium thiosulphate and then throwing them onto a pile. There would then be a sufficient start to the reduction to prevent any considerable diffusion of chromic acid into the reducing bath.

Chrome tannage, either by the one-bath or two-bath process, yields a leather having fixed both a strong acid, like sulphuric or hydrochloric, and a relatively weak base, chromic oxide. The free acid in the leather would prevent a good penetration of fat-liquor, made of an emulsion of oil in soap solution, which gives to chrome leather its substance; the emulsion would be destroyed and there would be no proper lubrication of the fibers. This explains why chrome-tanned leathers, at the end of the process, undergo an exact neutralization by means of a dilute solution of some alkali salt, such as borax, sodium phosphate, bicarbonate, silicate, or thiosulphate.

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Neutralized chrome leather can be freed also from chromic oxide by treatment with alkali salts of hydroxy-acids, like tartaric, citric, etc.[33]

Tanning with Syntans.

Stiasny[34] patented in 1912 the preparation and use as tanning agents of the condensation products of phenols with formaldehyde, in the presence of sulphuric acid. These products contain free sulphonic groups and are soluble in water. Their constitution has not yet been established with certainty, although it seems probable that a derivative of diphenylmethane is formed, which then polymerizes, increasing the molecular weight considerably and yielding a semi-colloidal product. The compounds thus obtained give solutions possessing a number of properties common to tannin solutions: they precipitate gelatin and give a blue-violet coloration with ferric salts. They have been designated "synthetic tannins" or "syntans."

The product sold before the war by the "Badische" under the name of "Neradol-D" was a condensation product of cresols with formaldehyde in the presence of sulphuric acid. Since the war began, several English firms have begun to manufacture these products.

The tanning action of these bodies is due to the *free* sulphonic and *free* hydroxy groups which are absorbed by the skin, thanks to their acid character. If the sulphonic and hydroxy groups be neutralized gradually, the tanning power of the product diminishes in proportion. The name "synthetic tannins" given to these bodies is therefore not quite justified. Moreover, they can be utilized only for preliminary tannages and their use up to the present has been very limited.

J. A. W.

University of Lyons, France.

[33] Procter and Wilson, *J. S. C. I.*, **35**, 156 (1916); this Journal, **11**, 173 (1916).

[34] French patent 443,730; U. S. patent 1,232,620. See also Dierdorf, *Collegium*, 1913, p. 366; this Journal, **8**, 394 (1913). Grasser, *Collegium*, 1913, p. 413; this Journal, **8**, 404 (1913). Eitner, *Der Gerber*, 1913, pp. 155 and 169; this Journal, **8**, 361 (1913). Moeller, *Collegium*, 1913, pp. 487 and 593; this Journal, **8**, 479 (1913). Stiasny, *Collegium*, 1913, p. 528; this Journal, **8**, 479 (1913).

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ABSTRACTS.

Thymolsulphophthalein as an Indicator in Acidimetric Titrations. A. B. CLARK and H. A. LUBS, Color Investigation Laboratory, Bureau of Chemistry, Department of Agriculture. *J. A. C. S.*, 40, 1918, pp. 1443 to 1448. Thymolsulphophthalein is a three-color indicator, the strong acid end of which is magenta, the weak acid end is yellow or orange, and the alkali end is blue. Starting with a strong acid solution the color changes from magenta to yellow at a hydrogen-ion concentration between 10^{-1} and 10^{-2} and changes from yellow to blue at a hydrogen-ion concentration of 10^{-8}. Using this indicator, it is possible to titrate a strong acid in the presence of a weak acid.

The following typical titrations are given. A mixture of benzoic acid and hydrochloric acid was made up as follows: Benzoic acid was dissolved in 50 per cent. alcohol. Definite amounts of this were mixed with known amounts of hydrochloric acid. Ten cc. of the benzoic acid solution dissolved in 40 cc. of water to which was added 1 cc. of a 0.02 per cent. aqueous solution of the indicator, was used as a standard. One cc. of the above indicator was added to every 50 cc. of the mixture to be titrated. The mixture was then titrated with normal sodium hydroxide until the exact color of the standard was reached. The titration was continued until the first trace of blue was reached. The first end point gave the hydrochloric acid content, and the difference between the first and second end points gave the benzoic acid content.

Mixtures of acetic acid and hydrochloric acid present more difficulties in that the hydrogen-ion concentration of these acids is more nearly the same. In this case it is best to run a preliminary titration on the mixture and then use the content of acetic acid found to make up your standard solution. This will give results, very near the theoretical.

Mixtures of sulphuric acid and acetic acid give accurate results only when the amount of acetic acid is small in comparison to the amount of sulphuric acid present.

Aniline hydrochloride or mixtures of aniline and hydrochloric acid can be titrated using the method used in determining acetic and hydrochloric acids. The aqueous solution of thymolsulphophthalein is prepared by placing 0.1 gram of the dry powder in a small weighing bottle and adding 0.25 cc. of normal sodium hydroxide and warming on the water bath a few minutes. After the indicator is dissolved, it can be diluted to the desired volume. Alcoholic solutions can be made by dissolving directly in 95 per cent. alcohol. Carbon dioxide should be excluded as it interferes with the accuracy of the determinations.

The Examination of Commercial Dextrin and Related Starch Products. F. W. BABINGTON, ALFRED TINGLE, and C. E. WATSON. *J. S. C. I.*, 1918, 15, pp. 257t and 258t. The authors are not satisfied with the method of Lamb and Harvey (*J. Soc. Dy. and Col.*, 1918, 34, 10; this JOURNAL, 1918, 7, p. 345). It includes as starch only insoluble starch while soluble starch

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is determined as part of the dextrin. They find that mixtures of starch and dextrin are hard to separate by filtration. The authors define starch as the group of carbohydrates which whether soluble in cold water or not, form a solution or gelatinize with hot water, give a blue color with iodine, and are precipitated by semi-saturating the cold solution with barium hydroxide.

By dextrin gum is meant the mixture which results from the hydrolysis of starch when the change has not been carried to a complete conversion to sugar. It gives no blue color with iodine, and is soluble in cold water and in cold semi-saturated barium hydroxide. The authors propose the following method:

One gram of the sample is warmed in a 100 cc. graduated flask, with 30 cc. of water until just gelatinized, and cooled quickly; 50 cc. of a cold saturated barium hydroxide solution is added slowly with shaking and the mixture diluted to the mark. Mix and filter through a dry paper and pipette 50 cc. into a platinum dish. Add two drops of a 1 per cent. phenolphthalein solution and neutralize cautiously with normal hydrochloric acid. Restore the pink color with one or two drops of barium hydroxide, add a weighed quantity (about 10 grams) of sand and heat on the water bath. Stir well when almost dry so as to expose the maximum surface, dry, transfer to a hot air oven and dry to constant weight at exactly 120° C. Dextrin gum is hygroscopic, so precautions must be taken while cooling and weighing. Ash at as low temperature as possible, stirring well, cool and weigh. The loss in weight during ignition is the dextrin gum in ½ gram of sample.

The method gives very concordant results. The principle source of errror is in adding too great an excess of barium hydroxide over neutrality. The authors recommend in addition the determination of moisture, ash, reducing sugars, and insoluble starch by Lamb and Harvey's method.

Drum Tanned Sole Leather. E. G. KEINER. *H. and L.*, Jan. to July, 1918. Drum tannage to be successful should save time, labor, and tanning materials. In Europe drum tannage has been carried out successfully for years. An outline of the European method is given below. Green salted hides are most commonly used. They should be drum washed before soaking. The hides should not be left too long in the limes and the limes should not be too strong as too much lime makes soft leather. Five to 10 pounds of lime per 100 pounds of green hide should be used, the limes should be about 70° F., and should be made new frequently. After unhairing and fleshing the hides are delimed. They are then colored for 2 hours in a weak sweet liquor. The hides are then hung in press handlers, ten vats to a system. The head liquor is 50° barkometer, being spent liquor from the drums. The quantity of liquor on the head is regulated by the quality of liquor coming off the tail. Rockers are not advisable as rocking causes loose grain. The hides coming out of the handlers should show about one-third tanned through. Temperature of the liquors

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here plays an important part. Too high temperature causes loose or drawn grain. Too low causes too plump leather and too slow tannage. The temperature should be a good summer one.

The drum system is two drums to each lot of hides. The drums should make about 7 to 8 revolutions per minute and should be about 9 to 10 feet in diameter and 7½ to 8 feet long. The principle of drum tannage is as little movement as possible and as high a temperature as the leather will stand without injuring the grain or fiber. The drums should start at normal temperature 65 to 70° F., finally ending around 95° F. The liquor in the first drum should be 75° bark. and in the second 120° to 140° bark. Use as much liquor as possible to help keep down the heat. In the first drum bisulphited quebracho extract which tans rapidly should be used mixed with a little oak, chestnut, hemlock, etc., but in the second drum, the proportions should be reversed. The tanning should be completed in 36 to 48 hours. After thorough tanning the leather is soaked three days in a weak liquor and bleached. Or it can be treated with extract, then tempered in vats, and finally bleached, oiled, dried and finished.

Analysis of One-Bath Chrome Liquors. CLAUDE SMITH and FINI ENNA. *J. S. L. T. C.*, August, 1918. When organic matter, such as glucose (beyond certain concentrations) or hide substance, is present in chrome liquors, there is considerable difficulty in making a volumetric estimation of the chromium by oxidizing with sodium peroxide, since on acidifying the solution after boiling, the organic matter reduces the chromic acid to a considerable extent, if not wholly, whereby doubtful results are the outcome.

In order to find a reliable and quick procedure for the works laboratory, various methods were tried.

(*a*) Oxidize the alkaline solution with permanganate until the pink color is permanent; destroy excess permanganate with alcohol, rinse into a flask (or filter), fill up to the mark, allow precipitate to settle and carefully drawn an aliquot part (Procter, "Pocket Book").

This method has two distinct disadvantages: the addition of alcohol must be done very carefully, since a minute excess will reduce the chromic acid, the solution becoming green as before oxidation; the alcohol might be largely diluted with water to prevent this. Furthermore, it takes a comparatively long time for the precipitate to settle, and quickness is the very essence of a works laboratory method.

(*b*) Attempts were made to remove organic matter by oxidizing with (1) dilute and (2) concentrated nitric acid and driving off excess acid by evaporating with sulphuric acid. This method failed insofar that it was impossible to oxidize the organic matter fully, and reduction took place on acidifying and heating.

(*c*) The liquor containing organic matter was heated with concentrated sulphuric acid, adding a drop of mercury (cp. Kjeldahl method) and then, after neutralizing, oxidizing with sodium peroxide. This method

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failed since it was almost impossible to re-dissolve the cake-like formation of the chromium salt.

Finally, the method presented below was adopted and has been successfully employed in the laboratory for some months:

Dilute the liquor to be analyzed so as to contain 0.8-1.1 grams of chromium per liter and of this solution place 25 cc. in a 400 cc. beaker, dilute to about 150-200 cc., bring to a boil, and add slowly a little ammonia till the latter is in excess; then boil for a few minutes, allow the precipitate to settle, and decant off the supernatant liquid through a filter (we use Whatman No. 1, 12.5 cm.). Add boiling water to the precipitate and rinse the whole on to the filter; when the liquid has gone through, fill the filter with boiling water, taking care to rinse the precipitate down into the cone of the filter; now pierce the filter and collect in a 300 cc. Erlenmeyer flask, rinse with 1.5 cc. concentrated hydrochloric acid, and oxidize with 2-3 grams of sodium peroxide. The solution should now occupy a volume of about 150 cc. There is a brisk effervescence, and on gently shaking the liquid it may assume a blue coloration, which is, however, quickly replaced by a brownish yellow. Now boil until no more oxygen is given off (absence of small bubbles), add excess sulphuric or hydrochloric acid, boil again for one or two minutes, and proceed in the usual way by adding 10 cc. of a 5 per cent. solution of potassium iodide, allow to stand for a couple of minutes, and titrate with standard thiosulphate solution. Between 12-16 cc. N/10 solution should be needed.

Part II.

The determination of the "basicity" of a liquor, *i. e.*, the determination of the empirical constitution of the basic salt in solution, has been given a good deal of attention, and whilst the principle in the methods employed is the same, the actual working methods differ widely. The handiest is no doubt that of Procter and McCandlish, in which the liquor is titrated with N/2 NaOH and phenolphthalein.

The method proposed below has been used for some time, and besides being very quick is sufficiently accurate for the works laboratory; one drop of N/10 caustic soda being sufficient to indicate the end point of the titration with absolute certainty:

The liquor is diluted so as to contain 0.8 gram or less of chromium per liter. Such a quantity—5 to 10 cc.—of the liquor is used which will not use more than 5 cc. of N/10 alkali. This quantity is placed in a 400 cc. beaker, the contents brought up to about 100 cc. with boiling water, and this solution titrated as quickly as possible with N/10 NaOH solution. The end-point is indicated by a grey-violet tint of the solution, which appears red when viewed through the sides of the beaker. The beaker should be placed on a white tile. Each cc. N/10 alkali equals 0.0048 gram SO_4. Four to 6 drops of a 1 per cent. alcoholic solution of phenolphthalein should be used.

A few comparative tests are submitted.

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Liquor No.	Calculated acid	Procter-McCandlish	Found acid modified
1	--	29.4	29.1
2	24.1	23.7	24.4
3	20.0	20.4	20.1

Some difficulty was had in obtaining agreement by the Procter-McCandlish method, whereas by the modified method good results were obtained.

Analysis of Single-Bath Chrome Liquors. A. HARVEY. *J. S. L. T. C.*, August, 1918. In determining the basicity of a single-bath chrome liquor it is first necessary to estimate both the acidity and chromium. For the former determination, the method of Procter-McCandlish is most frequently used, which consists in titrating a known volume of the diluted liquor at the boil with N/2 NaOH using phenolphthalein as indicator. The object of the present note is to show, that under certain circumstances this method may give somewhat misleading results.

In a case which came under the writer's notice, the liquor was basic to such an extent that chromium hydrate was precipitated on diluting the liquor with water. At the same time an analysis of the liquor by the ordinary methods indicated a basicity of 88.8. As is well known, a liquor of this basicity has no tendency to precipitate when diluted. On further examination it was found that an ammonium salt was present in the liquor, and it was thought that this might account for such peculiar analytical results. Subsequently it was ascertained that in the preparation of the liquor, chromium ammonium sulphate, $Cr_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, had been used in place of the usual chrome alum. The ammonium sulphate thus introduced into the liquor would influence the acidity determination thus:

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O$$

and during the titration with N/2 NaOH in the usual way ammonia was evolved as indicated by the above equation. In consequence, the volume of N/2 NaOH used included that required to decompose the ammonium sulphate, with the result that on calculating the basicity an abnormal figure was arrived at.

Such a difficulty can be overcome by estimating the ammonia by distillation and allowing for its equivalent of N/2 NaOH when calculating the acidity from the reading obtained in the Procter-McCandlish method. By so doing the correct basicity can then be calculated.

The presence of ammonium salts in single-bath chrome liquors should be ascertained and allowed for when calculating the acidity and basicity.

German Substitute Leather. *Commerce Reports.* In view of the forthcoming British exhibition of footwear and leather substitutes, it is of interest to learn that an exhibition of somewhat similar character was recently held in Frankfort, Germany. According to the *Frankforter*

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Angelegenheiten, the exhibition was given up mostly to the products of the Substitute Sole Co. of Berlin, which has an annual production, it is said, of 150,000,000 soles for old boots and 50,000,000 soles for new boots, and to the finished boots and shoes made by several manufacturers out of substitute materials. The statement is made that the number of such firms will undoubtedly increase, since the German people will be obliged to wear goods of this kind for several years after the war.

A variety of soles were shown. One line consisted of a mixture of old rubber, canvas, and felt, which possessed a certain amount of flexibility but very poor wearing qualities. A wooden sole which could be sewn and therefore used on better-grade shoes was a feature of the display. For use on coarser boots and shoes worn by laborers a metal-bound wooden sole has been developed; for miners and agricultural workers a thick wooden sole with a wooden waist and heel is provided. The latter was especially designed after a careful study of the anatomy of the foot, so that, in the lighter forms, it has been used successfully as a remedy for flat feet. The so-called "Agfa" sole appears to give the most satisfaction, although all of its ingredients are not known. The fact that nitroglycerine forms an important part in its manufacture, however, greatly limits its production on account of the need for that article in munitions making. The "Agfa" sole is said to become tougher in water, unlike leather, and therefore to possess very long wearing qualities. Toe caps and innersoles made of "Fulkan" fiber and "Granitol" were likewise included in the collection of substitutes.

In the same room was a display of German war-time boots made with a wooden sole, a paper upper, patent leather facings, and a paper waist. A metal sole has recently been adopted by certain regiments in the German Army, and a sample shoe equipped with this sole was included with the shoe display. The uses to which leather trimmings and offal is being put for both military and civilian requirements were also brought out at the Frankfort exhibition. It is the intention of the company to hold the exhibit in most of the important cities of Germany. In each city classes will be formed to instruct shoemakers in the most effective methods of applying the substitute soles.

Wattle Wood for Cask Making in South Africa. *Commerce Reports.* The South African Department of Industries has recently received information of an interesting experiment carried out with wattle wood. Two casks made in Durban from this material have so far stood the most severe tests as to durability. One of the casks was filled some two years ago with molasses and has been exposed to the weather during this period without showing the least sign of leakage. It is stated that for this purpose molasses proves a more severe test than spirit. It is also noteworthy that the wood used in the above experiment was neither specially selected nor seasoned. The subject is one worthy of further investigation, in view of the revived interest in the coopering industry.

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Anthrax Disinfection. Report of the Disinfection Committee. Govt. Rep. London: His Majesty's Stationery Office, 1918. *Journal Society Dy. and Col.*, July, 1918. The Anthrax Committee was appointed in 1913 to report on the revisions necessary in the Factory and Workshop Act to prevent the contraction of anthrax by those handling dangerous wool and hair. They found that for a number of years the Bradford manufacturers, acting on the advice of the Bradford Anthrax Investigation Board, had voluntarily carried out certain precautionary measures, but it was decided that these precautions were inapplicable to workers at the ports and elsewhere, and that a scheme of disinfection was the only real safeguard. A sub-committee was appointed to deal with the matter.

After exhaustive experiment and large scale trial, a process was adopted based on treatment of the raw wool with formaldehyde solution. It is probable that such treatment would have to be undertaken by the Government in specially constructed stations at the port of entry, and it is computed that the cost would not be more than 0.8 pence per pound.

The treatment consists of four stages:

STAGE 1.—*Preliminary Treatment.*—Passing slowly (20 minutes) through a modified scouring bowl containing a solution of soap and alkali at 100°-110° F., with occasional squeezing. This process removes or softens the blood clots, and the spores are rendered susceptible.

STAGE 2.—*Disinfection.*—The material is similarly treated for 20 minutes at 100° F. with a 2 to 2½ per cent. solution of formaldehyde. This machine must be boxed in.

At this stage the bulk of the anthrax spores are destroyed, only those surviving which are embedded in remnants of blood clots which have escaped disintegration during Stage 1.

STAGE 3.—*Drying* in a current of air heated to 160° F.

STAGE 4.—Standing for some days to ensure the complete destruction of the few remaining spores by the formaldehyde remaining in the wool.

The process as thus carried out has no appreciable effect on the quality or spinning properties of the material.

The large scale experiments were carried out on the scouring plant of the Bradford Technical College, which consists of three scouring bowls and a detached drier. The third bowl was boxed in and used for Stage 2 (disinfection), the first and second bowls being used for Stage 1. Special driving arrangements were necessary to run the bowls and drying machines at about one-tenth the usual speed.

The experiments were made on the under-mentioned lots, representing the dangerous classes of wool:

(1) 1,004 pounds Persian (Brown Bagdad) wool.
(2) 509 pounds Persian (Brown Bagdad) wool.
(3) 2,000 pounds Persian blends.
(4) 1,042 pounds mohair.
(5) 1,025 pounds alpaca.
(6) 600 pounds East Indian wool.
(7) 90 pounds low grade East Indian wool.

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Full details of each experiment are given in the report, along with reports from the spinners, etc., who worked the material up alongside untreated lots of the same materials.

The report extends altogether to 93 pages.

Adulteration of Leather in South Africa. *Commerce Reports.* One of the earliest questions submitted to the South African Industries and Advisory Board was that of the adulteration of leather in local manufacture. In 1914, mainly on the recommendations of the Trades and Industries Commission, the Legislature agreed to the imposition of a special import duty of 6d. per pound on adulterated leather entering the Union. Unfortunately the absence of restriction or penalty on the adulteration of leather locally manufactured has resulted in the production of much leather of this kind. The committee, therefore, recommends the following:

(1) Sole, kip, and harness leather, tanned by vegetable process, shall not contain more than 2 per cent. of anhydrous mineral matter and 1 per cent. of glucose (or sugars). The anhydrous mineral matter shall be reckoned as the ash remaining after the leather has been completely burned at a dull red heat (preferably in a muffle).

(2) Mineral and combination tanned leather shall contain not more than 1.5 per cent. of mineral matter in excess of that present as a tanning agent. That the foregoing formula be made to apply to the exportation from the Union of locally manufactured leather; also that the Government should take into consideration the desirability of passing an act to enable the foregoing formula to be applied to leather manufactured and sold within the Union.

(3) That the duty in respect of imported leathers which do not comply with the foregoing formula shall be 6d. per pound in addition to the amount of the ad valorem duty on pure leather.

The board states that its recommendation in regard to increased duty on imported adulterated leather is contingent upon the application of the suggested formula to locally manufactured leather.

Laundering Army Shoes. *S. and L. Reporter,* Sept. 19, 1918. Experiments in laundering shoes are being conducted at various camps by the conservation and reclamation division of the Quartermaster's Corps, following receipt of reports that this has been found to be practicable and successful by the American Expeditionary Forces.

The method employed on this side of the water is the same as used in France, a solution composed of 1 gallon of strong disinfectant to 50 gallons of water being used to wash about 200 Army shoes. Standard laundry machines are used. The solution is germicide, antiseptic and deodorant. After fourteen minutes washing, the shoes are removed, dried for about an hour and then resoled. The results were found to be highly satisfactory. After the shoes are laundered and repaired they are greased

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with dubbin to make them more pliable and at the same time to preserve the leather.

The satisfactory results obtained from these first experiments in laundering shoes has encouraged the conservation and reclamation division to extend its operations along this line to all the camps and cantonments throughout the United States.

Moellon and Sod Oils. E. G. KEINER. *H. and L.*, Sept. 7th. Natural moellons are by-products in the manufacture of chamois leather. Artificial moellons are made by blowing air through cod or fish oil. Representative analyses of the two oils are as follows:

	Natural	Artificial
Moisture	20 to 23	21 to 30
Unsaponifiable	1 to 2	0.5 to 16
Degras former	7 to 9	8 to 13
Free fatty acid	12 to 18	10 to 15
Ash	0.2 to 0.8	0.2 to 0.3

Both are being used with great success for softening and filling leather, particularly chrome tanned leather. Fish oil does not make as good a moellon as cod oil as it dries out on standing and causes spewing on the leather.

Sulphonated Oils. E. G. KEINER. *H. and L.*, Aug. 3, 1918. The author gives a description of the manufacture of sulphonated oil, a typical analysis of a good oil and some of the more common adulterants. He concludes with methods of using such oils both in the extract wheels and oiling and stuffing wheels.

Hot Grease on Dry Leather. E. G. KEINER. *H. and L.*, Sept. 21, 1918. The article describes a method of adding very hot or boiling grease to absolutely dry leather. When the sides come from the yard, they should be oiled while still wet with a good grade of cod oil on the grain side. The first drying should be done slowly in the ordinary manner. The sides should then be taken to an air-tight room having a temperature of 115° to 125° F. where they are hung until absolutely free from moisture. A side is then put on a sloping table, flesh side up, and hot grease (185° to 200° F.) added from a steam jacketed kettle. Enough grease should be added to penetrate the leather in the thinner parts which is shown by grease spots on the grain side. The grease is applied with a soft brush. To check the penetration of the grease the side can then be dipped in cold water. Or the sides after greasing can be piled until thorough penetration is obtained. This system is much better than dipping in hot grease, as it enables one to distribute the grease load better, and not overload the flanks and bellies. The dip system too cannot be used when colored leather is desired.

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PATENTS.

Fertilizer from Organic Matter. U. S. Patent 1,268,563. A. J. GRINBERG, New York, and B. FIELD, Plymouth, Mass. Organic matter (including leather) is treated with acid producing bacteria, either with or without the addition of a phosphate compound or a potash compound, and the whole allowed to act until the action of the bacteria is completed.

Fertilizer from Tannery Waste Liquors. U. S. Patent 1,269,189. V. H. KADISH. The fertilizing matter in waste sulphide liquors is precipitated out with acid and thus is separated.

Leather Impregnated with Synthetic Resin. U. S. Patent 1,269,292. J. MCINTOSH.

Process of Purifying Water. U. S. Patent 1,274,560. VALERIUS KOBELT, Berlin, Germany.

Leather Substitute. U. S. Patent 1,276,113. R. B. RESPESS, New York. A fiber saturated with a binder of rubber, balata, fish glue, silicate of soda, sulphur and linseed oil.

Waterproofing Material for Leather. U. S. Patent 1,277,242. H. R. MOSNAT, Kansas City. A mixture of a gum, turpentine, acetate of lead, sulphate of iron, lead monoxide, plumbago, asphaltum and oil of mirbane.

Artificial Leather, U. S. Patent 1,277,528. C. E. ARNOLD, assignor to E. I. du Pont de Nemours. A process for applying nitrocellulose.

Tannery Waste Disposal Process. U. S. Patent. H. W. TAYLOR, New York. The process of combining the alkali wastes and the tanning wastes so that both are neutralized.

Treating Waste Leather. British Patent 115,421. C. BENNERT. The waste leather which must first be treated to remove grease, etc., is hydrolyzed with dilute alkalies. The resultant products such as protalbinic acids are used in the textile industries.

Leather Stained or Mordanted with Titanium. British Patent 116,123. H. WRIGLEY, H. SPENCE AND P. SPENCE AND SONS, Manchester, England.

Treatment of Hides and Skins. British Patent 116,334. L. A. GROTH, Purley, England. Electric current is passed through the suspended and agitated hides and skins, both before and during tanning.

Treating Sewage. British Patent 116,580. T. CAMK, Worcester, England. An air lift for raising sewage sludge from a settlement tank into an aeration tank in the activated sludge process.

Synthetic Tanning Agents. British Patents 116,933, 116,934. J. Y. JOHNSON, London, England. Sulphonic acids and their condensation products are manufactured and used as tanning agents.

Synthetic Tanning Agents. British Patent 116,936. H. WADE, London, England. Condensation products of naphthol sulphonic acids with formaldehyde.

Leather Working Machine. British Patent 117,358. J. W. H. HALL, Leeds, England.

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Leather. British Patent 117,628. F. R. RUTTIMANN, Lucerne, Switzerland. Animal bladders are dried, tanned, dyed, stretched and fat-liquored.

Glycerine Substitute. German Patent 299,228. A solution of glue or gelatin is treated with soluble thiocyanate, a product is formed resembling glycerine in appearance and some of its properties. An example is 100 parts of potassium thiocyanate, 50 water and 300 of a 33⅓% solution of gelatine. Syrup, extracts, etc., can be substituted for the gelatine.

Tanning. German Patents 304,859 and 305,777. BADISCHE, ANILIN UND SODA FABRIK GERMANY. Products obtained by sulphonating naphthol and naphthalene compounds.

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A STUDY OF ONE-BATH CHROME LIQUORS.

By John Arthur Wilson.

In this issue is reprinted an article by J. R. Blockey on the "Investigation of One-Bath Chrome Liquors," in which he criticises the recent work of Thomas and Baldwin,[1] who state that the "basicity" ratio is both inadequate and misleading as the only criterion of the tanning power of a chrome liquor. Blockey is apparently not ready to accept this statement and points out that "basicity" does not deal with concentration. He admits, however, that dilution and the addition of acid or alkali produce changes in the composition of liquors not recorded by the ordinary methods for estimating "basicity." He also endeavors to interpret some of Thomas and Baldwin's results, but if the mechanism of the reaction of chrome liquors were so simple as his explanation would indicate, there would be little need for controversy.

It has long been suspected that chrome liquors are extremely complicated systems and persons carrying out research in chrome tanning are continually being confronted by new and temporarily inexplicable phenomena. Last year Wilson and Kern[2] found that it is possible to have two chrome liquors identical in "basicity" and chromic oxide content and yet the chrome in one may be on the point of precipitating, while the addition of a considerable amount of alkali may be required to start precipitation in the other, the difference between the liquors being due to differences in concentration of neutral salts, such as NaCl or Na_2SO_4. Not a few persons have believed that the concentration of chromic oxide and "basicity," taken together, represented a quantitative measure of the tanning power of a chrome liquor. To one holding such a belief the "basicity" value in many cases would be *misleading,* and as the only criterion of the tanning power of a liquor would certainly be *inadequate.*

The principle underlying the method which Blockey proposes for using the hydrogen electrode for determining "basicities" appears to me to have no foundation in fact, unless it is to be applied only to systems so constant in composition and behavior

[1] This JOURNAL, 13, 192 (1918).
[2] This JOURNAL, 12, 445 (1917).

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as to make the determination unnecessary. It assumes that the potential differences obtained are functions only of the "basicity" and concentration of chromic oxide. In their second paper,[3] Thomas and Baldwin show that it is possible to keep the "basicity" and concentration of chromic oxide constant and yet vary the potential differences, found with the hydrogen electrode, through very wide limits, simply by varying the neutral salt content. They show further that, after altering the concentration of any one of the components of a liquor, the potential difference obtained may not become constant for days; the "basicity" value appears not to be subject to this time-factor and hence Blockey's method would be subject to another serious defect.

In actual practice, if the conditions governing tanning, such as the proportion of water to hide substance, the concentration of each acid and salt, etc., could be made exactly the same for each pack, the "basicity" value would probably be of real service in control work; but, if these conditions could be maintained, it would not be long before the control would no longer be necessary.

Blockey appears to be laboring under the delusion that the peculiar variations in hydrion concentration found by Thomas and Baldwin are due simply to the varying degrees of hydrolysis of the chrome salt. In all probability the hydrion concentration does govern very largely the degree of hydrolysis, but there are other factors causing notable variations in hydrion concentration which can readily be demonstrated, but for which no completely satisfactory explanation has yet been given. For example, Thomas and Baldwin showed that the addition of sodium chloride to a chrome liquor caused a marked increase in hydrion concentration. This might be explained by saying that the salt increased the degree of hydrolysis of the chrome compound, were it not for the fact that the addition of sodium chloride to dilute solutions of pure sulphuric or hydrochloric acids produces corresponding increases in concentration of hydrogen ions. Neither can it be explained as altering the degree of ionization of the acid, for in many cases the hydrion concentration becomes greater than the total normality of acid. This action has been observed frequently, and since no entirely satisfactory explana-

[3] This JOURNAL, 13, 248 (1918).

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tion has been forthcoming, it has been designated simply, "The Neutral Salt Effect," and has apparently been shelved, awaiting further data. Thomas and Baldwin found also that adding sodium sulphate to a very dilute solution of sulphuric acid caused a decrease in hydrion concentration, but when added to a chrome liquor, it was found that as the concentration of sodium sulphate was increased the hydrion concentration at first decreased and then began to increase.

The complexity of one-bath chrome liquors is probably due to the independent operation of several factors, each of which may be simple enough in itself. From a study of the effect of adding different kinds and amounts of neutral salts to chrome liquors, Wilson and Kern (*loc. cit.*) attributed their results to hydration, since it was found that for equimolar solutions of different salts the precipitation point was greater as the degree of hydration of the salt was greater. The idea in this reasoning was that, if the salt combined with some of the water, this water would no longer be available as solvent. Naturally, if the amount of solvent were decreased and the amount of free acid kept constant, the actual concentration of acid would be increased and consequently more alkali would be required to start precipitation of the chrome. The work of Thomas and Baldwin indicates that, while this theory may explain the action of chloride salts upon chrome liquors, it is insufficient in the case of sulphates. Sodium sulphate raises the precipitation point of a liquor to a greater extent than does sodium chloride, but it actually causes a decrease in hydrion concentration. Miss Baldwin has suggested that, in the case of the sulphates, addition-compounds may be formed, which seems not unlikely in view of the large number of double sulphates known, as for example the alums. Moreover, the tendency to form addition-compounds appears to be related in some way to hydration.

The logical method of solving the problem would be to get first of all a clear understanding of the action of neutral salts upon pure acid solutions. That we know so little about the action of NaCl upon HCl solutions, for example, may surprise some, but it is a fact. Harned,[4] working with the hydrogen electrode, found that the hydrion concentration of 0.1M HCl is increased from

[4] *J. Am. Chem. Soc.*, **37**, 2460 (1915).

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0.092 to 0.1765M by the presence of 3M KCl. He says, "this points to the conclusion that the solution acts as if it were contracting, or that the volume of solvent has decreased." He found also that the addition of such salts as KCl and NaCl to 0.1M solutions of NaOH and KOH caused an increase in hydroxyl concentration.

Since more data on this subject is now being collected, it seems advisable to defer any further speculation until the new data is available. The subject, however, is so important in the matter of placing chrome tanning on a highly scientific basis that every leather chemist should do his utmost to co-operate, either by independent experiment or by discussion of the evidence already accumulated.

It is unfortunate that Dr. Thomas was called to France before he had time to interpret his experimental results, but we may hope that he will resume the work upon his return. Meanwhile, Miss Baldwin is carrying on some independent investigations which should prove both interesting and valuable.

(NOTE.—Blockey accuses Thomas and Baldwin of error in the matter of giving "basicity" values for the pure chromium sulphate solutions which they employed, but it is difficult to find grounds for his accusation. For example, he claims that the "basicity" value of chromic sulphate should be 0.633 and not 0.770 as given by Thomas and Baldwin, although Thomas and Baldwin state quite specifically that "for each one of these solutions the 'basicity' value was 0.770." Miss Baldwin assures me that the "basicity" values were obtained by the A. L. C. A. method for the several dilutions and were very carefully checked. The purest chromic sulphate that I have been able to procure during the past year has a "basicity" value greater than 0.770.—J. A. W.)

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THE EFFECT OF IMPURE KAOLIN ON THE DETERMINATION OF ACID IN TAN LIQUORS.

By Douglas McCandlish and Fred B. Lederer.

Certain vegetable tan liquors recently analyzed by the A. L. C. A. method for total acidity gave abnormally low results and investigation showed that an error had been introduced by the kaolin used in the determination.

The kaolin, described as "acid washed," was obtained from a firm which had supplied a uniformly satisfactory product for many years. The present lot, however, has either been imperfectly washed with acid, or has escaped acid treatment entirely and has an alkalinity which is manifest when used in connection with the settling of liquors, following precipitation with gelatine solution. The water extract of the kaolin does not give an alkaline reaction with phenolphthalein and is neutral to methyl-orange and hematine solutions. It contains a trace of magnesium carbonate, also an appreciable amount of iron and it is from these two impurities that difficulties arise. Attempts to determine the water soluble matter by the official method—digesting 2 grams of kaolin with 200 cc. of water at 20° C. for one hour—filtering and evaporating 100 cc. of the clear filtrate, were unsuccessful, as the finely divided kaolin passed through the filter paper causing a persistent opalescence even after repeated filtration.

A modification of the usual method—shaking 20 grams kaolin with 200 cc. water at 20° C. for 1 hour, and filtering—gave a brilliantly clear filtrate. The larger amount of kaolin on the filter paper evidently acted as a more efficient filtering medium and retained the very fine particles of kaolin. The water soluble matter amounted to 2 milligrams per gram of kaolin. This was not considered sufficient to prohibit its use in connection with acid determination although it is double the amount specified as permissible in the regulations governing the determination of tannin. Water soluble matter of any description must obviously be reduced to a minimum in the latter case, but in the former, it would seem that a small amount of soluble matter could not have any serious influence on the results. In passing it may be of interest to note that some Swedish filter papers were found to contain an appreciable amount of water soluble matter.

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The error caused by the use of this sample of kaolin for the determination of acidity of tan liquors may be judged from the results given in the table.

Cubic centimeters of N/10 acetic acid diluted to 250 cc. and shaken with 15 grams kaolin	Grams of acetic acid in 100 cc. of diluted solution	Grams of acetic acid found in 100 cc. after standing		Percentage error after	
		(a) 20 minutes	(b) 1 hour	(a) 20 minutes	(b) 1 hour
5	0.012	0.001	trace	92	99+
10	0.024	0 010	0.007	58	71
20	0.048	0.026	0.024	46	50
30	0.072	0.048	0.043	33	40
40	0.096	0.060	0.053	38	45
50	0.120	0.072	0.067	40	44

The stated volumes of N/10 acetic acid were diluted to 250 cc. with distilled water in each case, 15 grams kaolin added, the mixture shaken and allowed to settle. Portions of 25 cc. were withdrawn from each after standing (*a*) 20 minutes, (*b*) 1 hour, 50 cc. water added and titrated with N/10 sodium hydroxide using hematine indicator, containing ½ gram Grubler's hematine in 100 cc. 95 per cent. alcohol. The concentrations of acid (column 2 of table) are such as would be obtained from tan liquors containing 0.12 to 1.20 per cent. acetic acid, after diluting 10 times, this being the stage at which kaolin is added according to the official method.

The end-point was fairly well defined when the lower concentrations of acid were used, but was more difficult to observe as the concentration of acid increased. This probably causes the percentage errors to be somewhat irregular, where they might be expected to approach a constant. A similar set of experiments was carried out using an older sample of kaolin. In this case the acid found by titration agreed with the amount added in every instance. It was noticed that the neutral points of the titrations were more readily observed when the latter kaolin was used. The unsatisfactory end-point with the low grade kaolin was found to be due to the presence of a small amount of iron, which was dissolved in sufficient quantities by the stronger acid solutions to interfere with the characteristic color change of hematine. Upon adding the indicator to such solutions, instead of the ordi-

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nary yellow color of hematine in acid solutions, a brownish color is obtained. As the neutral point is approached during titration the color darkens and the final end-point is difficult to detect. This interference is produced by a very minute amount of ferric salt.

If present in sufficient quantity, it is important to note that a violet blue color is given by iron and hematine in acetic acid solution, which might easily be mistaken for the neutral point aimed at in the ordinary process of acidity determination. This may be readily demonstrated by adding a few drops of hematine solution to N/500 acetic acid containing 20 milligrams of ferric chloride per liter. A pronounced violet color develops immediately, and gradually fades on standing. The intensity of the color and its permanence are influenced by the concentration of the acid. With a given amount of ferric chloride the maximum and more permanent color is developed in dilute acid solution. Thus a solution of N/1000 acetic acid containing 20 milligrams of ferric chloride per liter develops a more stable color with hematine than a N/10 acetic acid solution containing the same amount of ferric chloride.

It seems probable that other salts of metals may also have an adverse influence on the indicator, as hematine is known to form color compounds with many metallic salts.

In view of our experience with this sample of kaolin it seems desirable that a kaolin to be used in connection with the determination of acid in vegetable or chrome tanning liquors should pass a test on the following lines: Shake 15 grams of kaolin vigorously with 250 cc. N/50 acetic acid and allow to stand 1 hour; withdraw 50 cc. of the settled solution and titrate with N/10 sodium hydrate, using hematine as indicator. A titration of 10 cc. and the characteristic end-point indicate that the kaolin is free from alkaline matter and sufficiently free from iron to permit its use for the purpose in view.

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INVESTIGATION OF ONE-BATH CHROME LIQUORS.*

By J. R. Blockey, M. Sc.

Use of the Electrometric Method.

In 1913, at the Leathersellers' Technical College, the writer carried out some work on the use of the electrometric apparatus of Wood, Sand, and Law, for the investigation of one-bath chrome liquors, but owing to transference to Leeds and the impossibility of getting hold of a complete electrometric apparatus, the whole of the work which had been planned could not be completed, and publication of the results was therefore postponed. The paper by Arthur W. Thomas and Mabel E. Baldwin[1] has reopened the question, and as their experiments differ somewhat in scope and results from those of the writer, it was thought useful to describe the latter in the hope that other workers, if not Thomas and Baldwin themselves, will be able to pursue the work on some of the lines suggested.

Thomas and Baldwin's experiments and results may be briefly summarized thus: the concentration of hydrogen ions was determined in a standard stock chrome liquor. The variations of this concentration were noted as the liquor was diluted, both immediately after dilution and after the diluted liquors had been allowed to stand for several days. The same was done with a solution of pure chromium sulphate. The concentration of the hydrogen ion varied in both cases as the liquor was diluted and curves were given showing these variations, plotting as abscissæ the number of times the liquors were diluted, and as ordinates the logarithms of the concentrations of the hydrogen ion. The logarithm was chosen instead of the actual number to give a better graphical representation. The basicity as measured by the proportion of Cr_2O_3 to SO_3 remains the same as the liquor is diluted, but the concentration of the hydrogen ion varies.

(The official method of the A. L. C. A. measures the basicity of chrome liquors as the ratio $\frac{Cr_2O_3}{SO_3}$. The basicity is the ratio of basic radical to acid radical found by dividing the percentage of Cr_2O_3 by the percentage of SO_3, or of Cl, carrying the quo-

* *J. S. L. T. C.*, **2**, pp. 205-212 (1918).

[1] This Journal, 1918, p. 192.

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tient to two decimal places. Provisional method for the analysis of one-bath chrome liquors: "A. L. C. A. Book of Official Methods," 1918, p. 34. In Europe it is more common to measure the basicity as the parts of SO_4 to 52 parts Cr. Thus in normal chromium sulphate, $Cr_2(SO_4)_3$, the basicity by the A. L. C. A. method is $\frac{152}{240} = 0.633$, and by the English method 144. In $Cr(OH)SO_4$, the values are $\frac{152}{160} = 0.95$ and 96 respectively.)

Because the hydrogen ion concentration varies as the liquor is diluted whilst the basicity remains the same, Thomas and Baldwin conclude that the determination of basicity by the usual methods is inadequate. "It is evident that a change takes place in a chrome liquor when it is diluted which is in no way indicated by the basicity value. Moreover, this change is a change in the concentration of a constituent which, according to the consensus of opinion, is a very important factor in the tanning process, namely, the hydrogen ion."

This reasoning appears to the writer to be slightly misleading, or at any rate to have overlooked one important feature. The usual basicity determinations estimate the proportions of basic to acid radicals, and do not deal with concentrations, whilst the electrometric method estimates the concentration of hydrogen ions only. By altering the dilution of the liquor it would be phenomenal if the concentration of the hydrogen ion did not vary. The mere fact that the hydrogen ion concentration does vary is no proof that the basicity as measured in the usual way is no criterion of the tanning properties. If a dilute solution of hydrochloric acid be taken, say N/10, and its hydrogen ion concentration be determined by the electrometric method, and then diluted to N/100 and the hydrogen ion concentration again measured, it will be found to be approximately 1/10 of its previous value, but this does not signify therefore that the properties of the hydrochloric acid have varied (apart from the question of concentration). Such determinations might be useful in another direction. For instance in the two cases of N/10 HCl and N/100 HCl, if the hydrogen ion concentration in the former solution were exactly 10 times that of the latter, then it could be said that

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the HCl was ionized to exactly the same extent in both solutions. If the concentration of hydrogen ions in the N/10 solution were such that 50 per cent. of the HCl molecules were ionized, and if the concentration of hydrogen ions in the N/100 solution were 1/5 that of the N/10 solution then the HCl in the N/100 solution is 100 per cent. ionized.

Similarly in the case of the chrome liquor the fact that the hydrogen ion concentration varies with dilution is no criterion in itself that the basicity estimation is not correct, but if the concentration of the hydrogen ion varies directly as the concentration of the liquor then it can be said that the extent of hydrolysis of the chromium compound or the extent of ionization is the same for different dilutions. Thus if in one case the hydrogen ion concentration be x and the liquor be diluted 10 times, and the new concentration of hydrogen ion be $\frac{x}{10}$, then it can be said that the chromium compound has not undergone any different hydrolysis or ionization by dilution. By comparing the concentration of the hydrogen ion with the dilution it should be possible to determine something of the nature of the hydrolysis of the chromium salt.

In attempting to compare these two things from the figures obtained by Thomas and Baldwin, one is met by the difficulty that the concentration of the hydrogen ions is not constant after dilution. If the hydrogen ion concentration be determined immediately the liquor is diluted and again at various intervals it is found that constancy is only reached after many days. Thus when a solution of pure chromium sulphate containing 137.60 grams Cr_2O_3 per liter be diluted to contain 13.86 grams Cr_2O_3 per liter, the concentration of H^+ immediately is 0.00372, whilst after 9 days it has risen to 0.00468 mole per liter. In all the cases of dilution of chromium sulphate the concentration of H^+ increases with time. With a stock chrome liquor of basicity $\frac{Cr_2O_3}{SO_3} = 1.076$ the concentration was almost constant. It becomes difficult therefore to determine the effect of dilution upon the extent of hydrolysis of the chromium salt, but several conclusions can be drawn. It appears from the figures of Thomas

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and Baldwin that with a solution of pure chromium sulphate the hydrolysis into sulphuric acid and a more basic salt increases with the dilution because the concentration of hydrogen ions falls less rapidly than the concentration of the chromium sulphate. This is true both immediately after dilution and after standing for 9 days. The same is also true of a stock chrome liquor. Thus the following table shows the effect of dilution in a stock chrome liquor from which it is evident that the hydrolysis proceeds to a much further extent as the liquor is diluted.

A. Grams Cr_2O_3 per liter	B. Conc. H^+ in mols. per liter
0.29	0.00024
2.89	0.00045
5.77	0.00049
11.55	0.00055
23.09	0.00068
230.9	0.00490

The influence of time on the extent of hydrolysis is of interest. With chromium sulphate solution the hydrolysis increases with time when the solution is diluted. It appears that when a chromium sulphate solution is diluted immediate hydrolysis occurs, but also that the hydrolysis is not complete immediately and that time is required to produce equilibrium. With the stock chrome liquor the hydrolysis was complete immediately on dilution and no change occurred after 7 days.

The effect of adding alkali or acid to a chromium sulphate solution and then allowing the solution to stand is on similar lines. The concentration of hydrogen ions, and therefore the extent of hydrolysis is lower immediately the alkali is added than when the solution is allowed to stand. It appears that the alkali first neutralizes the hydrolyzed acid and that the remaining chromium salt only hydrolyzes very slowly. Thus in one case the hydrogen ion concentration immediately after adding alkali to a chromium sulphate solution was only 0.00004, but it rose to 0.00129 in 6 days and to 0.00170 in 30 days.

The effect of the addition of acid is in the opposite direction, that is, the concentration of hydrogen ions is higher immediately after adding the acid than after standing for days. Thus in one

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case the concentrations were 0.04898, 0.02884 and 0.02042, immediately, after 6 days, and after 30 days, respectively. It appears that the addition of acid reverses the hydrolysis but that complete equilibrium is only reached after many days.

It is quite evident therefore that dilution, and the addition of acid or alkali produce changes in the composition of the liquors which are not recorded by the ordinary methods of estimating basicity.

It is unfortunate that certain errors in Thomas and Baldwin's figures make it impossible to draw any comparison between the basicity as measured by the ordinary methods, and the extent of hydrolysis as measured by hydrogen ion concentration. The main error referred to is that the basicities as measured by the ratio $\frac{Cr_2O_3}{SO_3}$ are not in agreement with the figures given by Thomas and Baldwin. Thus for $Cr_2(SO_4)_3$ the correct figure is $\frac{152}{240} = 0.633$, whereas Thomas and Baldwin give it as 0.770.

Starting from this figure all the remainder are thrown out. It is difficult to see how the error has arisen, unless the figure has been obtained by analysis, but on the other hand the other figures have been obtained by calculation and not by analysis. All the figures therefore under the column $\frac{Cr_2O_3}{SO_3}$ giving the basicities are incorrect. Perhaps Thomas and Baldwin will give the correct basicities so that it will be possible to compare them with the extent of hydrolysis.

A factor equally important with the effect of dilution and the effect of allowing the solution to stand is the influence of temperature on the liquor. If a solution of a chromium salt be warmed and cooled again and the hydrogen ion concentration be measured before and after heating, it is found that the heating considerably increases the hydrolysis. This runs parallel with the curious effect on the color which has been the cause of so much speculation. When chrome alum is dissolved entirely in cold water the resulting solution is violet, and if this violet solution be boiled the color changes to bright green. Many explanations have been given of this phenomenon. Some observers have

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stated that the tanning effects of the two classes of liquor vary, and this has given rise to a widespread opinion that chrome alum must be dissolved cold. When the chrome alum is made basic the difference in the color is not so marked, and some observers have stated that no appreciable differences exist between the two solutions when made basic. The difference seems to be entirely due to hydrolysis. The following table shows the differences between the green and violet solutions at different dilutions. The violet solution was made by dissolving pure potash chrome alum in cold water, and the green in boiling water. In columns 3 and 5 are given the potential differences in volts as measured by the electrometric apparatus, and in columns 4 and 6 the corresponding hydrogen ion concentrations.

1	2	3	4	5	6
Grams chrome alum per liter	Grams Cr_2O_3 per liter	Violet solution		Green solution	
		P. D.	H^+ conc.	P. D.	H^+ conc.
150	22.8	0.430	0.00277	0.365	0.0375
100	15.2	0.440	0.00186	0.370	0.0307
75	11.4	0.445	0.00152	0.375	0.0251
50	7.6	0.450	0.00124	0.380	0.0205
25	3.8	0.455	0.00102	0.390	0.0137
10	1.52	0.460	0.00084	0.400	0.00923
5	0.76	0.460	0.00084	0.405	0.00759

In each case the concentration of the hydrogen ion is more than ten times as high in the green solution as in the violet, thus showing considerably more hydrolysis in the former. This explains the differences between the effects produced by the green and the violet solutions of the normal salt on pelt. The green solution produces more swelling than the violet and generally acts as if it contained more acid.

The Color of Chrome Solutions.

The difference between the green and the violet solutions may be explained on the ionic theory. The color of solutions according to this theory is due to the combined effects of the various ions and dissolved molecules. The final color is an additive effect of the colors of the anions, the cations and of the unionized molecules, the color of each of which may differ from the others. Thus, cupric chloride is a brown solid which when dissolved in a small quantity of water gives a yellow solution. It may be

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assumed that in this case the cupric chloride is very slightly ionized, and that the yellow color is due to the unionized molecules. As the solution is diluted the color becomes greener and finally blue. The blue color is due to the copper ions, since in very dilute solution the cupric chloride will be almost completely ionized, and chlorine ions are colorless. The green color at moderate dilutions is due to the partial ionization of the salt and the green is therefore due to the combined effects of the blue copper ions and the yellow cupric chloride molecules.

With chrome alum a similar thing probably occurs. The chrome alum molecules are violet, or the same color as the solid salt. A solution made in the cold in which ionization only occurs to a small extent, as evidenced by the small hydrogen ion concentration, is a violet color due to the color of the undissociated molecules. When such a solution is boiled, hydrolysis and ionization proceed to a higher degree and probably few undissociated molecules remain. The green color is due either to chromium ions which are always green or to a different sulphate of chromium. The color changes might also be explained by Werner's scheme of hydrates. Thus of the two hydrated chromic chlorides $CrCl_3 6H_2O$, the violet one in which the whole of the chlorine can be precipitated by silver nitrate is represented by Werner thus: $[Cr(H_2O)_6]'''Cl_3$, and the green one, in which only one-third of the chlorine can be precipitated by silver nitrate, thus $[CrCl_2(H_2O)_4]'Cl.2H_2O$.

As the violet and green solutions are diluted, the differences between them become less marked. This is what one would expect if the difference in color is due to ionization, for the more the solution is diluted the further the ionization. That heat and dilution increase the ionization is apparent not only from the figures for hydrogen ion concentration obtained by the electrometric method, but also from the behavior of basic chrome liquors. The more a basic liquor is diluted the more readily does it precipitate. A liquor which is quite clear at high concentrations may become turbid when diluted or when heated, which points to increased ionization in both cases, and to the production of the more basic and more insoluble chromium salt.

That the green and violet solutions are not identical when made basic may be proved by parallel tests. If two solutions of the

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same concentration be taken, one green and one violet, and a solution of either sodium hydroxide or of sodium carbonate be added to each of them until precipitation occurs, it is found that the violet solution precipitates sooner than the green, so that even at the point where the liquors are too basic to be stable the basicity is different in each case.

If an equivalent quantity of sodium hydroxide be used instead of sodium carbonate, the precipitation occurs much sooner. That is, a liquor made basic by addition of sodium hydroxide is much less stable than one made basic by washing soda, and cannot be made as basic without precipitation; in fact by adding sodium hydroxide to chrome alum dissolved cold, precipitation occurs before the basicity has reached $96SO_4 : 52Cr$, corresponding to $Cr(OH)SO_4$.

The use of the electrometric method to determine the way in which the green and violet salts are taken up by pelt would be of interest, and a beginning was made on these lines. The potential differences were measured from time to time as pelt was left in the solutions. In both cases it was found that the potential difference increased when neutral pelt was first placed in the chrome liquor, showing that acid was absorbed more rapidly than basic chromium salts. With the violet solution the acidity as measured by the ratio $52Cr : xSO_4$ was almost the same after one day, whilst with the green solution the value of x was much lower; in other words, the green solution became more basic, which shows a greater and more rapid absorption of acid from the green solution.

The Use of the Electrometric Method for Estimating Basicity.

One of the most promising of the uses of the electrometric apparatus is in measuring the basicity of a chrome liquor. The method can be used to determine the proportion of Cr to SO_4, or in other words what is usually meant by basicity. The method depends upon the fact that no matter how the liquor has been made up, if it be boiled and then cooled down again the potential difference will be constant. Thus if two liquors be made up, one by adding washing soda to the violet solution, and the other by adding the same amount of soda to the green solution, the poten-

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tial differences will be the same if the final liquors be boiled and cooled down again. By taking liquors of known basicity and measuring the potential difference after boiling and cooling, it is possible to plot curves showing the relationship between the two. A curve can be made showing the relationship between the potential difference and the basicity of chrome liquors made by adding washing soda to chrome alum, the final liquors being made to contain 1.52 per cent. of Cr_2O_3. Of course liquors of different concentrations of chromium will give rather different curves, but the method should be useful in checking stock chrome liquors which are made and known to contain uniform quantities. Moreover small differences of concentration of chromium produce smaller variations in the potential difference than small differences of basicity. In works control therefore, where the barkometer or specific gravity of a chrome liquor may be taken as a rough guide to the concentration of chromium (assuming that fairly constant types of stock liquor are used), it would only be necessary to determine the potential differences by the above method and refer to one of a set of curves, to obtain the basicities sufficiently accurately for works control. The set of curves could be conveniently chosen to represent liquors of definite specific gravity, say at intervals of 10° Bk.

In a curve the potential differences themselves can be given as well as the corresponding hydrogen ion concentrations, but in works control it is sufficient to measure the potential differences without the trouble of calculating the hydrogen ion concentration.

The latter is calculated from the former by the following formula:

$$\text{Potential difference} = \left(0.283 + 0.0575 \log \frac{1}{C}\right) \text{ volt when a}$$

normal calomel electrode is used.

Thus the potential difference using the instrument on a N/10 HCl solution is 0.345.

$$0.345 = 0.283 + 0.0575 \log \frac{1}{C}$$

$$c = 0.0836 \text{ grs. H ion per liter}$$

showing that in N/10 HCl the HCl is ionized to the extent of 83.6 per cent.

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RECENT DEVELOPMENTS IN LEATHER CHEMISTRY.*

By Henry R. Procter, D. Sc., F. I. C.,
Emeritus Professor of the Chemistry of Leather Manufacture, Leeds University; Director of the Procter International Research Laboratory.

LECTURE I.

For the comprehension of advances in leather chemistry, some knowledge not only of the chemistry but of the anatomical structure of skin is required; but, as the latter has been fully described in text-books, it may be very briefly dealt with here. The part of the skin which is converted into leather consists mainly of interlacing bundles of white fibers identical with the connective tissues of the body, and, like them, composed of a tough jelly substance (collagen), which is easily converted into actual gelatine by boiling with water. Interspersed with these, and especially abundant near the outer surface, are yellowish so-called "elastic" fibers of a different chemical nature, insoluble in boiling water, which remain in the leather but appear to take no considerable part in the tannage. Neither the white nor the yellow fibers are really living cells, but cell-products apparently produced by flattened and elongated nucleated cells lying beside them.

In the living animal there is, outside the leather-hide and separated from it by a thin varnish of different nature, sometimes called the hyaline, a layer of living nucleated cells, which form the growing portion of the epidermis, and which as they multiply push the older cells away from their source of nourishment, the blood and plasma of the leather-skin, so that they gradually die and dry up, and finally are removed by friction or washing from the skin surface. From this growing epidermis-layer originate not only hair, horns and nails, but sebaceous glands clustering round and lubricating the hairs, and still deeper sudoriferous glands. Though the hair-bulbs and their accompanying glands are deeply rooted in the leather-hide they are always surrounded by a layer of epidermal cells, continuous with the surface epidermal layer.

Chemically these epidermis products differ in a very marked

* *J. R. S. A.*, Oct. 25, 1918. Delivered before the Royal Society of Arts, May 13, 1918, in the Cobb series of Lectures.

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way from the leather-hide, being nearly insoluble in hot water, and incapable of forming gelatine, but more or less soluble in alkaline solutions or under the influence of certain digestive enzymes. They are all, as far as possible, removed from the skin before tannage, so that it is needless to discuss their chemistry in further detail.

Collagen, the material constituting the bulk of the leather-hide is, as has been stated, closely related to gelatine, of which it is probably merely an anhydride. Gelatine appears to be one of the simplest proteids, its principal proximate constituent being amino-acetic acid (glycocoll), and it contains no groups having a benzene-nucleus. Hence, though a useful proteid food, it is incapable alone of supporting life, since it lacks some of the amino-acids, especially tryptophane, which are now known to be essential.

Fischer's recent researches on the proteids have proved that they consist of more or less complicated chains of amino-acids. An organic acid owes its acid properties to the presence of the carboxyl group $-C(=O)-O-H$, to the spare bond of which is attached some hydrocarbon or other organic group on which depends its special character. Thus acetic acid is simply CH_3COOH, butyric $CH_3CH_2CH_2COOH$, while stearic acid has a chain of sixteen CH_2 between the carboxyl and the terminal CH_3. Other acids may have OH groups on the chain or its branches (hydroxy-acids), or one or more phenyl groups C_6H_5 (aromatic acids), so that almost infinite diversity is possible.

Now in place of one of the hydrogen atoms united directly to carbon it is possible to substitute an NH_2 (amino) group; thus amino-acetic acid is $H_2N.CH_2.COOH$; or, looked at in another way, the acetic acid group, less H, is substituted for one of the H's in the decidedly alkaline ammonia NH_3, and the amino-acid is thus a substituted ammonia. The result is a body having both acid and alkaline properties, but very weak in both. Such compounds are called "amphoteric," and it is obvious that the acid head of one molecule can combine with the alkaline tail of another to form a chain; and in this way the proteids are built

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up. Such chains obviously have a carboxyl-group at one end an an amino-group at the other, and therefore like their constituent amino-acids have both acid and alkaline functions, and this fact accounts for much of their behavior in the tanning processes.

In preparing skins or hides for tannage the first step is the removal of the hair and epidermis-structures. This is still sometimes effected on sheepskins by a regulated process of putrefaction, in which enzymes produced by bacteria bring the epidermis into partial solution, and so loosen the hair. These enzymes, or "unorganized ferments," are much akin to the digestive principles secreted by the human body, and like these are often very specific in their action, digesting one protein and refusing another. Of course the ideal aim would be to have bacteria of which the enzymes only attack epidermis, and not the white fibrous tissues; and as putrefaction usually begins in the epidermal growing layer, such bacteria are probably at first in excess; but the skins are in anything but sterile condition, and among the mixed millions of bacteria present in a tainted skin there are usually some which attack and injure the skin-tissue itself. The solution of the epidermis is not wholly the work of the bacterial enzymes, but is assisted by the ammonia evolved from the skins by their action, and it has been shown that gaseous ammonia alone will loosen the wool before there is time for any dangerous putrefaction to take place.

A much more important method, and one in almost universal use for heavy hides, is that of treatment with milk of lime. Almost any alkali can be used to loosen hair, but lime has the preference, not merely from its cheapness, but because of its very limited solubility in water, which enables it to be used in great excess without danger, and with the advantage that the dissolved lime, which alone is active, is automatically replaced as rapidly as it is taken up by the hide. If soda were used in quantities equivalent it would produce enormous swelling, and, to obtain the same gentle effect as lime, would have to be almost continuously added in successive small portions, which would greatly increase the labor. From 7 to 14 days and about 6 per cent. of lime on the weight of the hides is required for adequate liming, but much more is often used.

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From quite ancient times pastes of lime and realgar, a crude red arsenic disulphide, has been used for the removal of hair, not merely from the finer skins but from the human body. It was shown by Böttger that the effect was not due to the arsenic, but to the calcium sulphydrate formed by its reaction with the lime, and equally good results were obtained from sulphydrate formed by passing sulphureted hydrogen into lime-milk. Unfortunately the mixture will not keep, and has never been largely adopted. More recently arsenic sulphide has been largely replaced by the much cheaper sodium sulphide, Na_2S; and any of these alkaline sulphide mixtures will reduce hair and epidermis to paste in a few hours without injury to the skin, even if applied in a concentrated form. More usually, however, they are merely added in small quantity to ordinary lime liquors, of which they quicken the action, and so lessen injury to the skin without materially damaging the hair, which is of commercial value. It is worth remarking that orpiment, the yellow arsenic trisulphide, can be quite satisfactorily substituted for realgar, and is often cheaper.

For fine skins, sodium sulphide has never quite taken the place of the arsenic mixture, as it makes a thicker and coarser skin. The cause of this is that, on solution in water, sodium sulphide is resolved into equivalent parts of sodium sulphydrate and sodium hydrate, and the latter has a powerful swelling action on the skin; and if lime is added a still further portion of sodium hydrate is formed. This effect is greatly lessened by the addition of an equivalent quantity of calcium chloride, which, by reaction with the sodium hydrate, forms common salt and sparingly soluble calcium hydrate.

Just as in the case of "staling" the bacterial effect is assisted by the chemical action of ammonia, so in practical liming, the chemical action which would otherwise by very slow is supplemented by the bacteria and their enzymes which develop in the liquor. While this bacterial action in the limes does, in some cases, lead to injury, it is much less dangerous than direct putrefaction, since many noxious organisms cannot develop in the strongly alkaline liquor. It is singular that when arsenic is used it has practically no antiseptic influence.

Very recently Dr. Röhm has patented a process in which hair is loosened, not by ordinary chemical means, but by the direct

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action of the enzymes obtained from the pancreas of animals, and for certain purposes the method seems commercially successful.

Some years ago Messrs. Payne and Pullman patented a process of quick liming, consisting in first treating the goods for 24 hours with a 1 per cent. caustic soda solution, which sufficiently swelled and penetrated them, and afterwards for 24 hours with an equivalent calcium chloride solution which replaced the caustic soda in the hide by caustic lime. The liming was sufficient and complete, but as the solutions were sterile to bacteria, the goods would not unhair unless they were previously treated in a putrid soak to allow of bacterial action. If the caustic soda be partially replaced by sodium sulphide, bacterial action is no longer necessary.

Though the primary object of liming is no doubt the removal of hair, it has other important and desired effects. The fiber, from its amphoteric nature, combines with the alkali and is much swollen; the fiber-bundles are split up into their constituent fibrils, thus increasing permeability and offering much larger surface to the subsequent tanning process; and more or less of the interfibrillary cementing substance is dissolved and removed. The latter effect renders the leather softer and more porous, and hence is advantageous or the reverse, according to the object in view. It is principally due to the bacterial enzymes, and is therefore regulated to a considerable extent by the age of the liquors and the length of treatment—fresh limes swell the fiber more and dissolve less than old ones.

The hide or skin as it comes from the limes, and after mechanical treatment (now mostly by machines) to remove the hair and epidermis, is a swollen mass of gelatinous fibers containing about 4 per cent. of lime, partly in chemical combination with the collagen. Before tannage, it is necessary to remove this alkali, which would interfere in many ways with the subsequent processes; and if a soft leather is required, not only must the swelling be reduced, but in most cases a further portion of the interfibrillary substance and any residues of epidermis-matter must be dissolved and got rid of. Mere washing with water will only very slowly remove the combined alkali, since the proteid salt merely hydrolyzes when the outer solution is nearly neutral,

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and must be carried out with water practically free of carbonic acid and bicarbonates to avoid precipitation of calcium carbonate in the hide, which is difficult afterwards to remove.

When a firm or only a moderately soft leather is required, the use of acids to decompose the hide-lime compound is now general. By far the cheapest agents are the "strong" mineral acids, hydrochloric and sulphuric, the former having the advantage of a very soluble lime salt. Unfortunately the amphoteric hide is as ready to absorb acids as alkalies, and is equally swollen by them, so that to get good results exact neutralization without excess of acid is imperative, and to secure this demands intelligent chemical oversight, and hence tanners have largely fallen back on the use of much more costly but safer "weak" organic acids. The sour taste and swelling properties of an acid depend on the concentration of hydrogen ions in its solution, and hence on the completeness of the ionization, and while hydrochloric acid is almost wholly ionized in dilute solution and all its acidity is exerted at once on the pelt, lactic and acetic acid are only ionized to a very small extent, and consequently swell little; but as the acid is consumed, a further portion ionizes and maintains ionic concentration so that in the end as much lime is neutralized as by an equivalent quantity of a "strong" or highly ionized acid.

It is, however, possible to use the "strong" acids with perfect safety if they are added in insufficient quantity completely to remove the lime, and the deficiency is made up with a weak acid; or to a sufficient quantity of the strong acid, the salt of a weak one such as sodium acetate is added so that in either case the operation is completed with the weak acid only.

In the case of sulphuric acid, as calcium sulphate is rather insoluble, it is best to use at once enough of the weak acid to complete the deliming, and afterwards to treat the solution with a calculated quantity of sulphuric acid to precipitate the lime as sulphate, and again liberate the weak acid, when the liquor can be used a second time with only a small addition of organic acid to make up losses. The economy is worth making, for even at pre-war prices, while 28 pounds of lime could be neutralized with sulphuric acid for 0.8d. the same work with acetic acid costs 10d., and with lactic acid 1s. 6d. Niter-cake, a crude sodium bisulphate which is now much recommended by the Government

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as a substitute for sulphuric acid for many purposes, is not suitable for deliming, as in addition to the large quantity of sodium sulphate which it contains, and which lessens the solubility of the lime sulphate formed, it is generally contaminated with traces of nitric and nitrous acids which discolor the leather.

In place of organic acids, boracic acid, which is extremely weak and quite incapable of producing acid swelling, is often used, and the cheap sulphurous acid from burning sulphur deserves more attention than it has received.

In many cases, a simple acid deliming is sufficient even for dressing leathers where extreme softness is not required, and it effects considerable economy in hide-substance as compared to the bacterial and digestive methods which must be later described. For this purpose the previous liming should be somewhat long, and conducted in moderately old and bacterial limes to ensure sufficient removal of the interfibrillary substance, and the acids used must be so weak as to produce a minimum of swelling while removing the whole of the lime. This is secured by the use of any weak organic acid, with the addition of sufficient of its neutral salt to repress still further the already weak ionization, according to the well-known ionization law. This can be done by using repeatedly, after strengthening with acid, liquors which contain the calcium salt of previous operations. Salts of weak bases with strong acids, *e. g.*, ammonium chloride, may also be advantageously used, liberating ammonia only, which has little swelling effect.

The older methods of removing lime and producing the required flaccidity of the skin, depend on the use of somewhat disgusting fermenting mixtures of pigeon-, or, still worse, of dog-dung. In these the lime is removed mainly by the amino-acids and amine salts, produced by bacterial action, while at the same time the interfibrillary substance and the residues of epidermis and cellular structures are digested and rendered soluble by the bacterial enzymes. The latter action is so strong in the ordinary "dog-puer" at a temperature at 80° to 90° F. at which it is generally used, that in a few hours the entire skin may be dissolved. Undesired bacteria, which are always present, are also apt both to stain the skin and to corrode its texture, so that with the most intelligent management the process is dangerous as well as dis-

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agreeable. It may be added that septic and pathogenic bacteria are not infrequent.

The first improvement of this crude method was made by Joseph Turney Wood, to whom we owe most of our knowledge both of the bacteriology and the chemistry of these processes, gained in the limited leisure of a strenuous business career. He prepared a mixed but otherwise pure culture of certain bacteria which produced the necessary depleting effect without injury to the skin, and a suitable culture-medium for it by peptonizing gelatinous matter by acids, in conjunction with ground bone, to supply the necessary phosphates. The preparation was produced commercially by him in conjunction with a German firm, and has been used under the name of "Erodin" with a considerable degree of success on calfskins. Wood also showed that a solution of enzymes prepared from puer liquor, with the addition of an amine salt to neutralize and dissolve lime, would produce a satisfactory puering without the presence of any living bacteria. About the same time the suggestion was made that the puer owed its effect to digestive ferments of the dog which had escaped destruction. As all these digestive enzymes are readily putrefiable, and the dog-dung is always kept in a wet condition some time before use, this did not seem inherently probable. But Wood showed that the action could not be due to pepsin, which only acts in acid media, while the working puer-liquor is always alkaline; but that conceivably the pancreatic ferments, which require alkaline additions, might have some effect, and his experiments with pancreatin, an impure trypsin enzyme, gave a somewhat imperfect puering. Wood did not at that time carry the matter further, though he protected the idea in an American patent, but later it was taken up by Dr. Röhm, who, by improved methods of preparation of the pancreas extract and the addition of ammonium chloride to solubilize lime, produced a mixture which under the name of "Oropon" has proved quite successful for calfskins, though for certain uses of sheep, goat, and lamb skins, the practical problem cannot be regarded as wholly solved.

After skins have been puered they are usually "drenched," to cleanse them and remove residual lime, and occasionally drenching is employed without previous puering. The drench liquor is simply an infusion of bran made with hot water and allowed to

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ferment either with the skins or before introducing them. The nature of the process has been thoroughly investigated by Wood, who finds that the carbohydrates are first converted into glucose by an enzyme, cerealin, which is naturally present in the bran, and that the glucose is further fermented by bacteria, lactic, acetic and carbonic acids and hydrogen being the principal products. The active bacteria are B. furfuris α and β (Wood), and are possibly originally derived from the puered skins. They are only active in very weakly acid liquors, and die out, without frequent change of medium, from the poisonous effect of the acids they produce, so that the process is, to a large extent, a self-regulated deliming, in which the concentration of the mixed acids is kept constant by their effect on the bacteria. The gases evolved have the effect of floating up the skins at intervals, which are a rough indication of the progress of the operation. The skins, when properly drenched, are white and soft, but no longer quite so flaccid as when they came from the puers. The process is best conducted at about 70° F., and if carried too far the gases evolved in the interior of the skins produce blisters and pinholes, and injurious fermentation from "wild" bacteria may also occur.

It is obvious, from what has been already said, that very much in the tanning process hangs on the property of hide fibers of swelling in acid or alkaline solutions, and "falling," or becoming thin, loose, and flaccid under other conditions; and I must try to give you some idea of what has been recently done to explain these effects, though I admit the subject is an extremely difficult one, and much of the work of myself and my collaborators has not yet found its way into chemical text-books.

I do not know whether I may assume that most of my audience are familiar with the ionic theory, and while time forbids any lengthy explanation, yet without it much of what I am going to say, sufficiently difficult in itself, will be entirely incomprehensible. If atoms are likened to small glass bulbs, each with a definite charge of electricity, positive or negative, sealed inside, it is obvious, on ordinary electrical principles, that the positive bulbs will attract and adhere to the negative, and this, in a very rude way, is a picture of ordinary chemical combination. If, however, such adhering bulbs are placed in a conducting liquid, such as water, their charges will be neutralized by opposite ones con-

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densed on their surfaces, and they will cease to attract each other and be free to move *in* the liquid, though they will recover their attractions if withdrawn from it. Water acts in this way, as an "ionizing liquid"—the negative Cl' and the positive Na^+ joined together in solid salt are free to separate within a sufficiently dilute solution; and as all atoms possess the violent vibratory motion we call heat, they tend to separate and diffuse, and exercise pressure, which is called *osmotic,* on the liquid surfaces which confine them. In any solution there is always a definite proportion of such free ions as compared to those which still remain combined, but in "weak" acids and bases, and especially in water itself, this proportion is a very small one.

There is a process known as "pickling," which has sometimes been employed for deliming and as a preparation for chrome and other tannages, as well as commercially, on a very large scale, for preserving wet sheepskins for export. This process involves both swelling and falling, and will in itself convert skin into a sort of leather, so that manifestly its full explanation would throw a good deal of light on the whole theory of tanning.

This process has occupied my attention at times for the last twenty years, and from it I have learned much and hope to learn more, for such an investigation never ends, but always opens up new and often unexpected problems, and the same causes which produce the pickling of sheepskins may be shown to be responsible for some of the most important actions in the human body, and, among others, in all probability for muscular contraction.

The pickling process essentially consists in swelling the skin with an acid, usually in practice sulphuric or hydrochloric (but any acid will do which will cause swelling); and then treating the swollen and gelatinous pelt with a strong solution of common salt in which it "falls," or becomes thin and white, and on being squeezed between the fingers can be wrung out like a rag. We have then a felt of unswollen fibers which do not adhere on drying, or at least may be easily separated by stretching, leaving a very complete white leather, which, however, if placed in water quickly returns to the condition of swollen pelt. I wanted to know why the fiber swelled in acids and why it shrank in salt solutions, for these were obviously fundamental questions in leather manufacture, and I began my work on sheets of gelatine

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instead of on actual skin, because they were chemically almost identical, while gelatine was uncomplicated by the capillary structure of the natural fibrous tissue, so that the actual swelling of the jelly itself could be accurately weighed and measured. I used hydrochloric acid for most of my experiments as a simple monobasic acid, identical with that contained in common salt. My first step was to determine the effect on swelling of gradually increased concentration of acid solutions, and at once a singular fact became obvious. The swelling did not increase proportionately to the concentration of the acid, but reached a maximum at a very low concentration (about 1 gram-molecule in 5,000 liters of water) and then steadily sank with increasing concentration to a point when the acid became strong enough gradually to break up the gelatine chemically, and the experiment could not be further continued. If, however, salt were substituted for further additions of acid no chemical breaking up occurred, and the shrinking could be continued till the gelatine became a horny mass.

When very small quantities of acid only are added to the gelatine it remains at first quite neutral to such indicators as methyl-orange or Congo-red, which react to free acid only, and the acid is evidently neutralized by the gelatine, or, in other words, has formed a gelatine-salt, though as more acid is gradually added there is no sudden change as there would be with soda or lime, and the indicator passes over quite gradually to the acid condition. In former times this was used as an argument that no really definite combination took place, but it is now known that with weak bases, such, for instance, as gelatine or alumina, the salt can only exist in presence of some amount of free acid, without which it breaks up again by combination with the elements of water to re-form the base and acid. Thus a solution of alum is always sour and contains free alumina, and its reaction to indicators is quite gradual.

We have now means of determining the free acid actually present in a given mixture, and as the process (hydrolysis) follows known laws, we can calculate the composition of the neutral salt, or, in other words, the weight of base which will unite with one equivalent of acid can be ascertained. I have calculated in this way the combining equivalent of gelatine as a base as 839,

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a large value, but much lower than had been previously supposed. The value is probably not quite accurate, but cannot be far wrong. This does not say that the actual molecule is only 839 times the weight of a hydrogen atom, but only that this is the weight of the smallest individual portion of the chemical substance, gelatine, which can exist. At ordinary temperatures, many such chemical individuals may be linked together to one large molecule by what is called polymerization, but it seems probable that as the boiling-point of a water-solution of gelatine is approached, 839 or some approximate value represents the actual molecular weight.

It must be understood then that every mass of gelatine jelly or every gelatinous hide-fiber in an acid solution of any definite strength is in equilibrium with the surrounding solution, that is that it contains water, gelatine salt, free gelatine, and free acid in such proportions that there is no tendency for either acid or water from the surrounding solutions to pass either into or out of the jelly, though both can pass freely through its surface.

In applying these facts to our problem we may simplify the task to a certain extent by neglecting the un-ionized substances, which in this case affect it only indirectly, and confining our attention to the ions themselves which are the real active agents.

If we admit the existence of gelatine salts, we have to consider the effect of their ionization on the swelling. The gelatine-ion remains colloid, that is, it tends to agglomerate into masses or large particles which do not diffuse, and consequently exert no appreciable osmotic pressure, while the ionized salt still remains a jelly or a colloidal solution. The Cl ion, on the other hand, tends to diffuse and exerts osmotic pressure, but cannot leave the jelly on account of the electro-chemical attraction of the gel-ion. It therefore swells the jelly, thus drawing into it the outside acid solution. This, however, contains the hydrogen and chlorine ions of the ionized acid in equal quantity, and while the former can enter the jelly without hindrance, the latter is opposed by the osmotic pressure of the ionized Cl already inside. The results are that the acid which enters is less concentrated than that outside, that the concentration of Cl within is greater, and that of H less in the jelly than in the outer solution, and as the acid H cannot enter without its associated Cl, a layer of positive H^+ forms outside

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the jelly surface, opposed and balanced by a similar layer of negative Cl′ within. Thus the two sides of the surface are in different electrical condition, or, in electrical language, there is a potential between them (Donnan's "Membrane Potential") and the surface layer outside the jelly has a small + electric charge. If, instead of being acid, the jelly and outer solution were alkaline, say with soda, the gelatine being amphoteric would form a sodium gelatinate in place of a gelatine chloride, and the charge would be negative instead of positive. It is obvious that between these conditions there must be an "isoelectric" point of neutrality at which there is no potential charge. This does not necessarily occur at the exact acid and alkaline neutrality of water, but is dependent on the relative acid and alkaline affinities of the individual proteid. In gelatine and hide-fiber, it is slightly on the alkaline side, and this is the point of minimum swelling and greatest flaccidity of the skin, and is generally approximately realized in bating and puering processes which have that aim. With regard to the actual tanning process, these charges are also of the highest importance.

The osmotic pressure tending to swell the jelly is therefore a balance of two opposing forces, that of H^+ pressing in, and of Cl′ (or some other acid-ion) pressing out. Donnan has shown that when the jelly and its outer solution are in electrical and chemical equilibrium, the proportions of the two are connected by the law that the H^+ multiplied by the Cl′ within the jelly must equal the $H^+ \times$ Cl′ of the outer acid. Now the H and Cl of the outer acid are equal, while in the jelly Cl is in excess, and the *sum* of equals is always less than that of unequals which give the same *product*. Thus the *sum* of $4 + 4$ is 8, that of $8 + 2$ is 10, yet both give the *product* 16. There is thus always a slight osmotic force tending to swell the jelly, greater as the two factors are more different. The greatest difference occurs when the quantity of free acid is very small and the chlorine in the jelly is almost entirely in the form of gelatine salt, and it is there that we get the greatest swelling. As the concentration of the acid and its quantity in the jelly increases the difference becomes less and the swelling diminishes, and if we add salt also in large excess, as in pickling, both almost entirely disappear.

We have therefore accounted for the swelling force, and shown

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that as it increases or diminishes the swelling does the same, and not merely in a general way, but mathematically and quantitatively, and that this force only quite disappears when the concentrations become infinite and equal. As, however, the swelling does not go on to infinity and solution, there must be some opposing force, which, when the swelling reaches a definite equilibrium, is equal and opposite to the swelling force. This is apparently the attraction of one gelatine particle for another, the elastic cohesion of the gelatine; and it seems to follow the Hooke's law generally applicable to elastic strains, in that it is proportional to the volume-extension. The exact nature of such strains has not yet been determined, but in the case of colloids it may have much to do with surface tension. That it is sufficient to account even for the intense contraction under the influence of salt is shown by its magnitude when water is withdrawn by ordinary evaporation—a drying film of gelatine will often actually tear away the surface of glass to which it adheres. In another respect it resembles other elastic forces, since it diminishes rapidly and the swelling increases with increased temperature till at the melting-point of the jelly it apparently disappears, and the swelling goes on to complete or colloid solution. As, however, even in solution, the gelatine particles can be shown to retain their electric charges, it is probable that at least at temperatures below 70° C. they still continue as separate particles suspended in a surrounding liquid.

LOG BARK.*

The Forest Products Laboratory has completed experiments on a commercial scale which indicate that the hemlock bark, wood free, obtained in paper mill operations, can be successfully dried and used as a source of tannin. These experiments were undertaken some six months ago, in co-operation with a group consisting of the Marathon Paper Mills Co., Rothschild, Wis.; the Bayley Manufacturing Co. and the Pfister & Vogel Leather Co., both of Milwaukee. In 1915, similar work was initiated by the Forest Service, but conditions at that time were not favorable to the success of the problem.

* Contribution from the Forest Products Laboratory, United States Department of Agriculture.

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The utilization of this waste bark is particularly important in view of the probable shortage of tanning materials as a consequence of the scarcity of labor in the woods, the gradual exhaustion of hemlock trees suitable for peeling, and the high freight rates to the tanning centers.

It is hoped that a plant operating on a commercial scale will soon be converting this former waste into a valuable product, at a cost which should leave a satisfactory margin of profit for the paper mill owner.

ABSTRACTS.

American Sumac. F. P. VEITCH, Chemist in Charge, and J. S. ROGERS, Assistant Chemist, Leather and Paper Laboratory;[1] U. S. Dept. of Agriculture, Bulletin No. 706. Sumac grows wild on uncultivated lands in a large part of the United States, and is especially abundant and accessible east of the Mississippi River, from Maine to central Georgia and Mississippi. Plentiful stands are found on cut-over land, in old fields, in pastures, on mountain sides, in waste places, and on the edges of swamps in the Appalachian region. Immense quantities of this valuable tanning and dyeing material, which costs nothing to raise, remain ungathered in this country every year, while vegetable tanning materials to the value of more than $5,000,000[2] are imported annually. If the sumac industry were well organized, the large quantities of this native tanning and dyeing material now wasted could be utilized in making leather and as a substitute for other dyes wherever practicable. This would serve to check the rising cost of similar tanning and dyeing materials, to lessen our dependence on foreign countries, and to give the country people in certain sections an additional source of employment.

Sumac has long been used in the tanning of leather and in dyeing fabrics. Its value for tanning depends chiefly upon the fact that it yields durable, light-colored or white leathers, and, consequently, it is used largely in the tanning of bookbinding, glove, and hat band leathers, and for removing darker-colored tanning materials from the surface of bag, case, and fair harness leathers. Sumac-tanned leathers have been found to be most durable and suitable for bookbindings and other purposes, where the leather must last indefinitely. The greater part of the gathered Americau sumac, however, is used for dyeing cotton goods.

The sumac industry in the United States is of direct interest to the country people of certain sections. It is largely a farm industry, since the

[1] The writers wish to acknowlege the assistance of R. W. Frey of the Bureau of Chemistry in the chemical work connected with this investigation.

[2] Foreign Commerce and Navigation of the United States, 1916, U. S. Dept. of Commerce.

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sumac is harvested and cured by the country people, and is sold through country dealers for grinding or for the manufacture of sumac extract.

In recent years the quantity of sumac harvested has been relatively much smaller than formerly. Cheaper materials for making light-colored leathers are in use, while the demands of dyers have not been large. American sumac, owing to careless gathering and curing, yields a darker-colored leather than the sumac imported from Sicily, and, since sumac is used for tanning light-colored leathers, this quality renders the American product less desirable for this purpose and decreases the demand for it. Another reason for the small amount collected is that the gatherers often earned less than could be made at other kinds of work.

Investigations with a view to the betterment of the conditions of collection and the improvement of the quality of American sumac indicate that the re-establishment of the sumac industry in this country on a firmer basis is entirely possible, and is especially desirable at this time, when the importation of Sicilian sumac is restricted by difficulties of transportation.

American sumac, if properly handled, will make an excellent substitute for Sicilian sumac. Consumers of sumac must realize, however, that the first step necessary for the production of a high-grade sumac similar to the foreign article is proper gathering and proper curing, which can be accomplished only by offering as an incentive to the country people a price commensurate with the quality. The better the sumac the better should be the price. In this way mutual benefit will be gained, and much will be done toward materially developing the domestic sumac industry.

Statistics probably do not indicate accurately the quantity of sumac gathered in the United States, because careful records are not kept by gatherers and dealers of the amounts collected and used. The figures for domestic production given in Table I were compiled from the Census reports, and the figures for the imports on the reports on commerce and navigation of the United States, issued by the U. S. Department of Commerce.

TABLE I.—Production of Sumac in the United States.

Year	Sumac extract		Ground sumac	
	Quantity Pounds	Value	Quantity Pounds	Value
1899	3,349,742	$103,085	9,284,000	$114,660
1904	4,093,619	95,958	5,061,333	65,190
1909	3,148,790	107,456	———	———
1914	4,512,361	129,631	———	———

Information in the possession of the Bureau of Chemistry shows clearly that the consumption of domestic sumac during the two or three years prior to 1917 has been more than 10,000,000 pounds annually. Early in 1910 domestic sumac was quoted at $55 per ton. Sicilian sumac is now (May, 1918) worth from $102 to $105 per ton at the chief Atlantic ports. Domestic sumac recently (May, 1918) was quoted at $60 per ton.

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TABLE II.—IMPORTATION OF SUMAC INTO THE UNITED STATES.

Year	Sumac extract (imported for consumption)		Ground sumac (general importation)	
	Quantity Pounds	Value	Quantity Pounds	Value
1894	1,277,609	$54,535	8,383,570	$192,647
1899	1,266,542	48,399	12,975,970	183,136
1904	1,356,020	50,681	18,604,644	276,891
1909	1,232,830	54,171	10,974,613	293,249
1910	1,461,373	54,899	13,632,861	299,170
1911	987,348	36,025	———	———
1912	1,389,733	46,551	12,498,376	235,154
1913	1,270,825	44,568	14,489,776	297,506
1914	1,029,792	42,973	10,770,400	258,738
1915	727,449	35,066	13,165,182	323,448
1916	36,003	4,108	21,542,390	555,276
1917	———	———	11,637,023	365,173

Important species of sumac growing in North America are: Dwarf sumac (*Rhus copallina* L.), white sumac (*Rhus glabra* L.), staghorn sumac (*Rhus hirta* (L.) Sudw.). Other species which contain tannin are: Fragrant sumac (*Rhus aromatica* Ait.), American smoke tree (*Rhus cotinoides* Nutt.), coral or Jamaica sumac (*Rhus metopium* L.). Two species of sumac are poisonous, namely: Poison sumac, or poison elder (*Rhus vernix* L.), and poison or three-leaf ivy (*Rhus radicans* L.).

Descriptions of the characteristics, together with the geographic distribution, of the more important species follow.

DWARF SUMAC, sometimes called BLACK or MOUNTAIN SUMAC (Rhus *copallina*).—A shrub or sometimes a small tree with maximum height of 30 feet and trunk diameter of 10 inches. The leaflets are dark green, smooth on top, paler and often hairy underneath, with edges smooth or few-toothed toward the apex. The fruit grows in dense terminal clusters, is crimson in color, and is covered with fine hairs. The unmistakable characteristic of this species is the peculiar winged growth along the leaf stem between the leaflets. Dwarf sumac grows in dry soil, and may be found from Maine and southern Ontario to Florida and Texas, and west to Minnesota and Nebraska.

WHITE SUMAC, sometimes called SMOOTH, UPLAND, or SCARLET SUMAC (*Rhus glabra*).—A shrub, or rarely a small tree, 2 to 20 feet high. The leaflets are dark green on top with whitish underneath, with edges sharply saw-toothed. The fruit grows in dense terminal clusters, and is covered with short reddish hairs. The distinguishing characteristics of this species are the smoothness of the stalks and leaf stems, together with a bluish white bloom, a powdery film similar in appearance to that found on plums, which covers them and the under side of the leaflets. White sumac grows in dry soil from Nova Scotia to British Columbia, and south to Florida, Mississippi, and Arizona.

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STAGHORN SUMAC, sometimes called HAIRY SUMAC (*Rhus hirta*, L.).—A shrub, or small tree, with maximum height of 40 feet and trunk diameter of 9 inches. Leaflets, dark green and nearly smooth on top, pale, and more or less hairy underneath, with edges sharply saw-toothed. The fruit, which grows in dense terminal clusters, is thickly covered with bright crimson hairs. The distinguishing characteristic of this species is the hairy growth along the stalks and leaf stems. Staghorn sumac is found in dry and rocky soils from Nova Scotia to Georgia, especially among the mountains, and as far west as southern Ontario, Minnesota, Missouri, and Mississippi.

Since poison sumac sometimes is mistaken for the more common species, and its poisonous effects are usually very severe, it seems desirable to describe it as an aid in distinguishing poison sumac from the other species.

POISON SUMAC, sometimes called POISON ELDER (*Rhus vernix*, L.).—A shrub, or small tree, with maximum height of 28 feet and trunk diameter of 6 inches. The leaflets are green on top and underneath, with edges smooth. The fruit, which grows in loose, open clusters, consists of smooth white or light gray berries. It should be noted that poison sumac differs decidedly from the important species in the color and cluster formation of its fruit. Furthermore, it may be easily distinguished from the dwarf sumac by the absence of the winged growth along the leaf stems, and from the white and staghorn sumac by its smooth-edged leaflets. Poison sumac almost invariably is found in swamps. It grows from southern Ontario and near the eastern coast in the Eastern and Middle States, south to Florida, and west to Minnesota, Missouri, and Louisiana.

Sumac is commonly termed by the gatherers either "black" or "white." "Black" sumac refers to dwarf sumac (*Rhus copallina*), and "white" sumac usually means white sumac (*Rhus glabra*), although it is believed that this term is sometimes applied also to staghorn sumac (*Rhus hirta*). *Rhus hirta* is not so extensively gathered as *Rhus glabra*. In some sections, as in eastern Virginia, only the dwarf sumac is collected, while in others, such as the western part of Virginia and in West Virginia, Maryland, and Pennsylvania, both dwarf and white sumac are gathered.

In eastern Virginia the dwarf sumac only is accepted, other species being positively refused. All contracts with gatherers specify that the sumac shall be of the dwarf species only. The leaves, leaf stems, and new growth of stalks if broken immediately below the lowest leaf stem are acceptable. The reason given in eastern Virginia for not receiving the white species is that it contains a much larger proportion of pithy, milky stalks, and yields less extract.

In western Maryland, Pennsylvania, and West Virginia, and, in fact, generally in the sections which supply northern mills, the leaves and leaf stems of all varieties, mixed or unmixed, are equally acceptable.

Extract makers are opposed to the early gathering of sumac, even though the leaves apparently are mature. They state that the leaves

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gathered in May and June are light weight, do not yield as much extract, and cannot be handled as well in the extracting process. From the viewpoint of both gatherers and extract makers, the best time to gather sumac is in July, August, and September. Gathering may be continued until frost. The dropping off of the leaves, however, constitutes a loss, while the color of the extract made from red or poorly cured leaves is darker and less desirable than that made from light-colored, well-cured leaves.

While sumac is very plentiful, especially in the eastern United States, it rarely covers thickly an area of any extent, but, intermingled with other vegetation, grows rather scattered in patches along old fence rows, and on cut-over and burned-over woodland. Reports have been received that in certain sections it grows thickly, unmixed with other growth, and in sufficient areas to permit cutting with a mowing machine. Several cases of clean stand have been reported, but they have not come directly to the attention of the Bureau of Chemistry. A report has been received from eastern Virginia of a tract of from 10 to 15 acres of burned-over and cut-over land from which 5 tons of dwarf sumac (leaves, leaf stems, and current year's stalk) were gathered. An estimate by the bureau, based on the material gathered from a measured area 20 by 30 feet of white sumac, gave a calculated yield of 4,864 pounds (green weight) per acre. This would give about 1,621 pounds of cured sumac.

Many factors may influence the quantity a man can gather. Some of these are the experience and alacrity of the gatherer, availability or lack of teams for hauling, growth of sumac—whether dense or scattering—species of sumac collected, and whether leaves, leaf stems, and stalks, or only leaves and leaf stems are desired. The amount of sumac collected by one man in one day may weigh from 150 to 600 pounds when dried, but averages between 200 and 300 pounds. From experiments conducted by the bureau, in which the sumac was collected by an experienced gatherer, it has been estimated that the following amounts of sumac (leaves, leaf stems, and stalks combined) can be gathered in one eight-hour day by an energetic man, provided the stand is good, so that little time is lost in going from one patch to another:

Dwarf—728 pounds green; loss of water in curing, 54 per cent.; cured sumac, 335 pounds.[8]

White—1,744 pounds green; loss of water in curing, 67 per cent.; cured sumac, 576 pounds.

Staghorn—952 pounds green; loss of water in curing, 58 per cent.; cured sumac, 400 pounds.

Where the stand is scattering or the gatherer is slow, the quantity gathered will be less, but in no case should an able-bodied man be satisfied with less than 200 pounds of cured sumac (leaves and stalks) from his day's work.

The general practice followed in gathering is to break or cut (only the black can be broken readily) the new-growth stalk just below the

[8] The dwarf sumac was more scattered than the other two varieties. This may account for the comparatively low figures for this species.

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lowest leaf stem. The sumac is then allowed to wilt in the sun for a few hours or a day, and hauled to a barn, where it is spread on the barn floor in a layer of from 1 to 3 feet in depth, or on racks which permit the circulation of air underneath. The sumac is then turned once or twice each day for a week to aid in the drying and to prevent the leaves from molding. Some gatherers do not let the sumac wilt in the sun, but spread it at once on racks in the barn or under cover. This method aids materially in producing sumac of the lightest and best color.

Experienced gatherers estimate that the green sumac loses from 50 to 60 per cent. in weight during curing. There is still further loss in weight between the time of purchase by the dealer and the time of sale, due largely to loss of moisture, still present because of incomplete drying, to falling of leaves, and to the removal of adhering dirt. This loss between the purchase and sale by the dealer varies in amount from 5 to 15 per cent., thus making a total loss in weight from the original green sumac of from 60 to 75 per cent.

Results of laboratory experiments on the curing of sumac (leaves, leaf stems, and stalks) given in Table III show losses while curing which agree well with those estimated by gatherers.

TABLE III.—Loss of Moisture in Curing Sumac
(Collected Sept. 28, 1916).

Species	Duration of drying (Days)	Loss of moisture (Per cent.)
Dwarf	5	50.5
	25	53.2
	49	53.6
White	5	63.9
	25	66.1
	49	66.6
Staghorn	5	55.5
	25	57.3
	49	57.8

There is reason to believe that the loss in curing on the farm is not so great as the loss observed in the bureau's experiments, where the sumac dried out very thoroughly. The total loss in weight of the mixed leaf and stalks from gathering until it reaches the extract maker probably averages very close to 60 per cent.

Sumac received by the dealers from the farmers usually comes in bags, or is handled loose in wagonloads like hay, and in many instances may have been hauled as far as 20 miles. Many farmers prefer to deliver the sumac in wagonloads, as they claim that too much time is consumed by putting it up in bags. Since the sumac becomes very brittle when dried and the leaflets are easily broken from the leaf stems, much loss occurs in handling it loose. Dealers, therefore, as a rule, prefer to have the sumac delivered in bags. These bags cost the dealers 8 to 9 cents

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each, but are usually furnished without cost to the gatherers. Some gatherers, after drying the sumac, flail off the leaves and pack them in bags for shipment. Seventy-five pounds should be packed into a 4-bushel bag, but the average quantity put into them is about 40 pounds.

From the small dealers to the extract manufacturers the sumac is usually handled in bags or bales. The cost of baling is about 10 cents per hundredweight.

During the seasons of 1916 and 1917 in eastern Virginia the gatherers received from 90 cents to $1 per 100 pounds in trade from the dealers. The extract manufacturers furnished bags for use in hauling and shipping the cured sumac. The dealers received from the extract makers $1.10 per 100 pounds for the bagged or baled material, which in this region includes the new-growth stalks as well as the leaves and leaf stems. In northern West Virginia and western Maryland the gatherers received in 1916 for the leaves and leaf stems alone (no stalks) from 80 cents to $1 per 100 pounds in trade from the dealers, who in turn received $1.10 to $1.15 from the extract makers. In 1917 these prices were about 5 cents per hundred higher. In this section all varieties of sumac are mixed and well packed for shipment in bags furnished free of charge by dealers.

The leaves and leaf stems together of the three most important American sumacs—dwarf, white, and staghorn—when air-dried, contain approximately the same amount of tannin—that is, from 25 to 35 per cent.[4] The leaves of fragrant sumac are said to contain 13 per cent. tannin, of American smoke-tree 21 per cent., and of coral sumac 8 per cent. Usually the quantity of tannin appears to be somewhat greater later in the season than in June and early July. The leaves contain the highest percentage of tannin after they are fully grown and before they begin to turn yellow or red.

Analyses made in the Leather and Paper Laboratory of the Bureau of Chemistry of various samples of sumac gathered in Virginia, West Virginia, Maryland, and Pennsylvania gave the following results:

TABLE IV.—TANNIN CONTENT OF SAMPLES OF DWARF, WHITE, AND STAGHORN SUMAC.

	Tannin in leaves and leaf stems			Tannin in stalks		
Species	Average Per cent.	Maximum Per cent.	Minimum Per cent.	Average Per cent.	Maximum Per cent.	Minimum Per cent.
Dwarf	28.95	35.03	19.46	7.77	9.94	5.09
White	25.14	28.08	21.35	6.84	7.30	6.19
Staghorn	27.66	30.59	21.53	7.07	8.09	6.45

Dwarf sumac, it will be seen, contains somewhat more tannin than staghorn or white sumac. This bears out in a general way the statement of buyers in eastern Virginia, though this difference is of itself not great enough to justify the refusal of the white. The sumac samples analyzed were found to average 73.3 per cent. leaves and leaf stems and 26.7 per

[4] These figures apply more particularly to Virginia, West Virginia, Maryland, and Pennsylvania sumacs.

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cent. stalks. The variation, however, was marked, extending, in the case of the leaves and leaf stems, from 54 to 89 per cent., and, for the stalks, from 11 to 46 per cent. The large proportion of stalks indicated by the percentage last given should never be permitted. Gatherers must be careful to break the stalk close to the lowest leaf stem, and not to gather the long stalk bare of leaves. If the stalks are broken close to the leaf stems, the sumac will usually meet the buyers' demands. Dealers and extract makers very properly insist that the sumac as delivered shall not contain on an average more than 25 per cent. of stalks.

The portions of the plant usually considered of value for tanning and dyeing purposes are the leaves and leaf stems, although, as shown in TABLE IV, the stalks contain from 5 to 10 per cent. tannin, an amount entirely too large to discard after the trouble and expense of collecting and hauling to market has been incurred. This tannin should be recovered, as an extract could be made from the stalks and off-colored leaves that would be satisfactory for tanning and dyeing purposes when color is not the primary consideration.

Some extracts made from American sumac show the same results upon analysis as those made from the best Sicilian sumac, and contain coloring matter not more than 20 per cent. in excess of that found in Sicilian sumac extracts. They can be bought at about three-fifths the price paid for extracts made from Sicilian sumac.

Formerly the users of domestic sumac bought the leaves or ground sumac, which is the sumac leaf ground to a coarse powder, and made their own liquors for tanning or dyeing from these materials. In recent years the grinding of sumac has decreased, and users have bought sumac extracts instead. The price of domestic sumac extract, which contains usually about 25 per cent. of tannin and is sold on the basis of its tannin content, has increased materially in the past three years. In 1914 the quoted price per pound was about 3¾ cents; in 1915, from 3¾ to 9 cents; in 1916, from 5½ to 10 cents; in 1917, from 4½ to 5 cents; and at present (May, 1918), the price is 4½ to 5 cents per pound. A pound of extract contains approximately the same amount of tannin as a pound of sumac leaf, if anything somewhat less than a pound of the properly gathered and cured leaf.

In making sumac extract the tannin is extracted with large quantities of water which must be evaporated in expensive copper pans under skilled supervision and at some expense for fuel. When the extract is to be used, as much or more water than was evaporated in making it is added to secure a tanning or dyeing solution of the desired strength.

So far as can be learned, no really useful method of disposing of the extracted leaves is in general use. The material is placed in large piles or ricks, or used to fill in waste places. A small quantity is used on farm land as a top-dressing to be plowed under. Analyses of the commercially extracted material given in Table V show its fertilizing value.

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TABLE V.—Fertilizing Value of Commercially Extracted Sumac Leaves and Leaf Stems and Stalks.

Sample No.	Part of plant	Moisture Per cent.	Ash						
			Total Per cent.	Calcium oxide Per cent.	Potassium oxide Per cent.	Phosphorus pentoxide Per cent.	Total Per cent.	Calcium oxide Per cent.	Potassium oxide Per cent.	Phosphorus pentoxide Per cent.
32479	Leaves and leaf stems	5.70	1.66	0.11	0.23	5.13	32.36	2.14	4.48
32482	Leaves and leaf stems	5.33	1.95	0.09	0.20	5.32	36.65	1.69	3.76
32479	Stalks	4.59	1.31	0.39	0.15	3.43	38.19	11.37	4.37
32482	Stalks	4.59	1.44	0.17	0.11	3.24	41.36	5.24	3.39

Examination of a number of unextracted sumac samples gave: Ash, 4 to 7.5 per cent.; potassium oxide, 1.18 to 2.15 per cent. The ash of these samples contained from 25 to 30 per cent. of potassium oxide.

Comparison of the percentage of potassium oxide (K_2O) in the original material and in the water extract, as obtained for the tannin analysis, shows that although the unextracted sumac contains rather high percentages of potassium oxide, as is to be expected, this is almost entirely removed on extraction. These experiments were made on finely ground sumac leaves and leaf stems, whereas in commercial practice the extraction generally is made on the unground leaves and stalks, and consequently is not so thorough, especially in the case of the large stalks. This practice of making extraction on the unground leaves and stalks undoubtedly accounts for the comparatively high percentages of potassium oxide in the samples of commercially extracted stalks, analyses of which are given in Table V.

Except for the organic matter which it contains, extracted sumac has comparatively little value for the farmer. However, in sections where sumac is gathered, where the land is usually deficient in organic matter, the extracted material can be profitably hauled a mile or two, especially if before scattering on the land it can be mixed and rotted with barnyard manure.

Lack of care and attention to details in gathering and curing results in sumac of inferior quality. Undue exposure to the sun or any exposure to dew or rain while green, and heating and molding resulting from too deep layers and insufficient turning during curing, cause a decided darkening of the leaves and materially reduce the percentage of tannin. The presence of stalks and red leaves in cured sumac is objectionable, because they produce an undesirable color on leather. Furthermore, since the stalks contain only about one-fourth as much tannin as the leaves, their presence gives the mixture a lower tannin content. The presence of dirt or sand in cured sumac also is objectionable, for it increases the weight without increasing the tannin content, and leathers tanned with such sumac will darken because of the iron present.

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One of the objects of this bulletin is to point out the necessity for helpful co-operation between gatherers, dealers, and extract makers, with a view to the production of higher-grade sumac and sumac extracts and the payment of higher prices to the gatherers for better sumac. This co-operation can be successfully maintained only if it is mutually beneficial. The initiative and success rest with the final buyers, the extract makers, who, by offering a bonus for "extra" quality sumac, can encourage the gatherers to make special efforts to produce a high-grade, bright, clean product. It is suggested that dealers and buyers keep on hand suitable samples, one to be known as "Standard," for which they will pay the regular price, and another as "Extra," for which a bonus of 15 to 30 cents per hundred will be paid, for the information and guidance of gatherers. Sumac materially below "Standard" in color or quality should be bought only at a reduction. If the directions for gathering and curing given in this bulletin are carefully followed, no sumac below "Standard" will be produced, while much of it will be of "Extra" quality.

In order to obtain sumac of the best quality, both as to color and percentage of tannin, carefully follow these directions:

Gather only dwarf, white, and staghorn sumacs. Break the stalk bearing the leaves and leaf stems just below the lowest leaf stem; or, better, gather only the leaves and leaf stems. Harvest during June, July, August, and September, and avoid the collection of red or yellow leaves. As soon as gathered, place the sumac in the shade or under a canvas cover, which permits the air to get to it, and avoids undue exposure to the sun. Do not allow it to be wet by dew or rain, and at the end of each day haul the gathered sumac to a barn or open shed, where it should be spread in layers not over 1½ feet deep upon a clean floor, or upon open racks which will permit ready access of air. Turn the layers over once or twice daily for from one to two weeks, or until thoroughly dry. In case the leaves have been gathered with stalks, separate these from the leaves and leaf stems by flailing and forking out. Do not allow the gathered sumac to come in contact with the bare ground at any time, as dirt injures the quality. The leaves thus prepared should be of a uniformly light green color. Pack tightly in bags and keep in a well-aired, dry loft until sold.

Sumac, when properly cured, usually can be sold to merchants in towns or cities near the place where it has been gathered; or it can be sold directly to manufacturers who buy sumac for grinding or for the preparation of sumac extract. Before starting to gather, however, the gatherer should have a definite understanding and contract with the dealer as to the quantity which he will buy from him; the price which will be paid; how the sumac is to be delivered; arrangements for a supply of bags, if it is to be delivered in bags; and especially as to the extra price to be paid for exceptionally bright, well-cured sumac. If the names of dealers are not obtained by inquiry of merchants, hide dealers, or others in nearby towns or cities, this information can be obtained from the various State agricultural experiment stations or from the Bureau

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of Chemistry, United States Department of Agriculture, Washington, D. C.

Sumac grows wild and abundantly on uncultivated lands, particularly east of the Mississippi River. Country people, especially the elderly and women and children, can make good wages from June to September by gathering and curing sumac. Imported sumac is scarce and high priced. Domestic sumac, if properly gathered and cured, can be largely substituted for imported, and should bring better prices than domestic sumac as now cured.

Before beginning to gather sumac be sure to arrange fully and clearly with the dealers as to: (1) The quantity which they will buy from you; (2) a supply of bags; (3) the price per 100 pounds; and especially (4) *an extra price for well-cured sumac leaf.*

Practically the only kinds of sumac gathered in this country are dwarf (*Rhus copallina* L.), white (*Rhus glabra* L.), and staghorn (*Rhus hirta* (L.) Sudw.).

Domestic sumac as now prepared for market contains less tannin, and is much inferior in color to imported Sicilian sumac.

Properly gathered and cured domestic sumac leaf contains from 25 to 30 per cent. of tannin, practically as much as Sicilian sumac leaf.

Owing chiefly to low quality, due to careless gathering and curing, the gatherer has received in recent years a low price for sumac, from 60 cents to $1.10 per 100 pounds. Carefully gathered and properly cured Sicilian sumac leaf sells in this country at from $2.50 to $4 per 100 pounds.

A better product, both in color and tannin content, is obtained by proper gathering and curing and by the separation of the stalks.

Domestic sumac extract, containing 25 per cent. of tannin, in 1914 sold at about 3¾ cents; 1915, from 3¾ to 9 cents; 1916, from 5½ to 10 cents; 1917, from 4½ to 5 cents; May, 1918, 4½ to 5 cents per pound.

The development of the American sumac industry and the production of bright, uniformly and properly cured domestic sumac can be accomplished only through the earnest and whole-hearted co-operation of the buyers and the gatherers. The buyers must make every effort to stimulate the proper gathering and curing by offering better prices and through careful instructions in proper methods of gathering, curing, and packing. The gatherers must respond by following exactly the directions set forth in this bulletin and the instructions and advice given by the buyers.

Gatherers should consult their State experiment station for the names and addresses of buyers of sumac and of sumac extract makers.

Tanning Materials in Germany. From *Le Soir* through *La Halle aux Cuirs*, Sept. 8, 1918. Some interesting information has come to hand concerning the use of Neradol in Germany as a tanning agent. This product tans rapidly and it is presumed that without it the scarcity of tanning materials in the central empires would be much greater than it has been since the beginning of the war. Its use, however, requires cer-

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tain precautions; some skins are not suited for use with it and the leather tanned with it disintegrates sooner or later. The minister of war at Vienna has forbidden its use in Austria. In Germany the complaints of its bad effects have become so great that the Leather Society for War would have taken the same measure, but a compromise was brought about through the intervention of the Badische Aniline Works, which possesses a monopoly on its manufacture and which sold in 1916 14,000,000 kilos at 55 marks per kilo. Tanners are now required to use from 25 to 30 per cent. of the quantity they used formerly. In order to compensate themselves for the loss arising from decreased sales of Neradol, the Badische has raised its price from 55 to 90 marks per kilo. It has also tried to sell it as a tanning extract under the name of "Tanol."

For some time Neradol has had the drawback of holding a certain proportion of sulphuric acid in the leather, which, when coming in contact with perspiration, produces a strong irritation on the skin. A new product, "Neradol-X," does not show this difficulty.

J. A. W.

Shoe Dubbing. The Quartermaster's Department of the U. S. Army has issued a circular asking for the manufacture of dubbing with the following formula:

50 parts neutral wool grease.
20 parts A, B, or C petrolatum.
10 parts paraffine wax (M. P. 118° to 121°).
20 parts water.

The commercial wool grease to be used is to contain not more than 3 per cent. of moisture and 2 per cent. of ash, and should be neutral.

Niter Cake as a Substitute for Sulphuric Acid. J. B. CHURCHILL, American Leather Research Laboratory. *S. and L. Reporter,* Oct. 24, 1918. In a report to the Tanners Council the author has gathered detailed data as to the production of this material in the United States. The quantity is almost unlimited. Analysis of many samples show this niter cake to contain from 26 to 40 per cent. acidity expressed as free sulphuric acid. Same can be obtained at a cost of from $2 to $9 per ton f. o. b. the shipping points, which are scattered throughout the country.

Letters from various tanners indicate that niter cake has been used successfully in bleaching sole leather, for deliming previous to chrome tanning, for pickling and storage of skins and as a substitute for sulphuric acid in the making of one-bath chrome liquors.

In the use of this material attention is called to its large sodium sulphate content. Allowance should be made for this whenever making up mixtures which should contain sulphuric acid and salt.

Rapid Determination of Resins in Soap. V. FORTINI. *Annali. Chim. Appli.,* 1918, 9, 102-108; *J. S. L. T. C.,* Sept., 1918. Twitchell's method of determining rosin soap has the drawbacks that it shows an apparent

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rosin content with pure soaps, and that it is not applicable to resins other than colophony. These drawbacks are obviated in the following method, which is based on the fact that nitrated resins are insoluble in petroleum spirit. Two grams of the mixed fatty and resin acids from 25 grams of the soap is treated in a separating funnel with 50 cc. of petroleum spirit (boiling point 40° to 70° C.), the presence of resin acids being indicated by incomplete solution. Ten cc. of nitric acid, prepared by mixing 25 cc. of fuming nitric acid (specific gravity 1.52) and 75 cc. of ordinary nitric acid (specific gravity 1.48) and adding a few crystals of urea to destroy nitrous acid, is then introduced in successive small portions. The mixture is shaken for 2 to 3 minutes, then allowed to stand, the acid layer drawn off, and the petroleum spirit shaken with an additional 5 cc. of the nitric acid, which is also drawn off. The petroleum spirit layer is then washed successively with ordinary nitric acid, and with water and filtered, the filtrate evaporated, and the residue of fatty acids dried and weighed. The quantity of resin acids is obtained by difference. The results thus obtained agree within about 1 per cent. of theory in the case of mixtures of 5 to 20 per cent. of rosin with saturated fatty acids or oleic acid.

Quinone Tannage I. (Continued). W. MOELLER. *Coll.*, 1918, 93-105; *J. S. L. T. C.*, Sept., 1918. Quinone is very easily oxidized by aqueous permanganate solution forming humins of high molecular weight exactly as all vegetable tannin solutions do. In all cases, colloidal complexes are obtained of unknown composition and of undoubted tanning properties. Scharwin has shown that quinones of high molecular weight, viz.: anthraquinone and phenanthraquinone had no action on proteins. Most theories of the quinone tannage claim that only those quinones with active oxygen are capable of tanning and dyeing, whilst according to the author's theory, only those quinones which can form colloidal peptized solutions in aqueous form, are capable of tanning. Anthraquinone has no action on hide either in aqueous or other solvents. Products containing anthraquinhydrone give weak tanning effects of quite a different nature to that of ordinary quinone. Phenanthraquinhydrone has only a weak tanning action on pelt, and the product can hardly be called leather. These experiments show that the far reaching polymerization and oxidation processes usually associated with quinone and its homologues only take place with great difficulty with anthraquinone and phenanthraquinone, and that colloidal peptized solutions are only produced under very special conditions. The quinone character of the phlobaphenes is related to this question as they easily split off multinuclear quinones and are difficult to oxidize to colloidal humins as do the simple quinones or the peptizers which consist of polyphenols. Tetrachloroquinone and duroquinone are very dissimilar to quinone in tanning action; they have not the tendency to form colloid complexes. Chloranil has no tanning action on pelt, but a trace of alkali added to a suspension in water converts some into chloranilic acid which has a strong peptizing action on the rest of the chloranil. This forms a quinhydrone which gives humins on further oxi-

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dation. Such a chloranil suspension treated with alkali has a much greater action on pelt than all the quinones previously investigated.

If pelt is treated with dilute aqueous solution of α-diketone and then with very dilute caustic solution, aldolization ensues and further condensation to *p*-xyloquinone. There is no special tannage unless the pelt is left longer in the liquor so that the precipitated quinones may be converted into colloidal peptized solutions. Aldol gives a small portion of amorphous isomer which can tan pelt giving a leather exactly similar to formaldehyde leather. The author thus traces a direct connection between the aldehyde and quinone tannages.

If ordinary quinone was stable in aqueous solution and formed no colloidal solutions it would have as little tanning action as anthraquinone. When benzoquinone has been converted into humins, only peptizable substances are present, and no peptizer, with the result that it has no tanning action. But these humins have a very strong tanning effect if they are peptized by fresh additions of benzoquinone or quinhydrone, thus confirming the first assertion of the author's theory that only peptized solutions can tan, but not the peptizer or the peptized substances alone. If the peptization equilibrium is disturbed and the peptizer completely destroyed by oxidation, the tanning effect ceases to exist. The peptizers of the vegetable tannins consist of polyphenols which are easily oxidized to humins, while the peptized substances are stable multinuclear quinones of high molecular weight which are not easily oxidized. If the air oxidizes the polyphenols into quinone-like humins, the equilibrium is disturbed, the phlobaphenes are precipitated and there is a darkening in color owing to the adsorption of the humins formed from the peptizer (polyphenols). The author considers that benzoquinone does not give a true quinone tannage, but a humin tannage whilst the quinonic phlobaphenes represent the true quinone tannage. The peptizer in vegetable tanned leather is capable of oxidation to quinones and hence humins are formed and this change going on in the leather is the cause of the deterioration of vegetable tanned leathers.

A Study of the Oxidation of Linseed Oil. G. E. HOLDEN and L. G. RADCLIFFE. *J. S. D. C.*, July, 1918, 138-146; *J. S. L. T. C.*, Sept., 1918. Experiments were carried out by subjecting 1 gram of linseed oil to a current of air, the oil to be spread over pieces of cotton cloth 3 inches square and these suspended in each of a series of bottles, air being drawn until a maximum increase is observed. After 500 hours, the gain in weight was 17 to 18 per cent., but on heating, this gain of 17-18 per cent. was lowered to one of 3 per cent. Curves showed, first, a very slow weight gain, followed by a rapid increase in each case. Manganese and lead resinate and linoleate used as driers, only produced the same result; but whereas without driers the maximum increase was attained after 300 to 600 hours, driers produced the same increase in 21 to 24 hours. Six times as much metallic lead as manganese was needed in the linseed oil solution to attain an equivalent drying efficiency. Turpentine used as

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a diluent in 10 per cent. proportions, caused a slight acceleration in the rate of drying. The action of heat on the oxidation of linseed oil was next studied by spreading 0.1 to 0.125 gram of oil on roughened glass plates measuring 7 by 7 inches, and heating these to different temperatures.

EXPERIMENTS ON ROUGHENED GLASS PLATES.

Wt. of linseed oil	Temp.	Max. increase	Per cent. increase	Time in hours
1.01	15 C.	0.176 gr.	17.4	119
0.99	34 C.	0.165 gr.	19.5	56
1.231	100 C.	2 hours 7.9%	—	Max. increase 6 hours 2.7%
Linseed oil 0.11 and manganese 1.210	100 C.	1½ hours 7.75%	—	1.1%
Linseed oil 0.989	150 C.	Loss after 1 hour 10.3%	—	Loss after 6 hours 23.5%

The higher the temperature, the quicker was the rate of drying, but a lower maximum increase in weight was observed, and in the case where driers were used, a lower efficiency of their action was noted. Volatile compounds were evolved during drying, and at higher temperatures the loss of these was greater than the gain in weight by absorption of oxygen. Twenty-five per cent. of the dried oil film was soluble in ether. Oils showing the lowest iodine value required longer time to dry than those showing higher iodine value, and the higher percentage of ether-soluble portions were dissolved from the films of the oils of lower iodine value. Saturated glycerides seemed to retard the rate of drying of the oils. Under the action of bright light from a 220-volt quartz mercury lamp, linseed oil dried as quickly as linseed oil containing a drier in solution, for in 4½ hours, it reached a maximum increase of 12 to 14 per cent. Acrolein was proved to be one of the volatile compounds evolved.

Estimation of Chromium in the Presence of Iron. K. SCHORLEMMER. *Coll.*, 1918, 145; *J. S. L. T. C.*, Sept., 1918. The presence of iron in solutions of chromium salts adversely influences the estimation of chromium in those solutions when they are oxidized and titrated with thiosulphate. The iron is dissolved up by acidifying, and the ferric salt thus formed reacts with potassium iodide to liberate iodine, thus giving too high results. If the iron is filtered off after oxidation the results are too low because the iron precipitate carries down some chromium with it and firmly retains it. The quantitative estimation of chromium must be done by oxidizing the solution, allowing to cool, and re-oxdizing after a fresh addition of peroxide; the ferric hydroxide is filtered off, dissolved in acid and twice oxidized with peroxide. The iron is filtered off from this

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second solution, and all the chromium is obtained in the two filtrates as chromate which can be estimated by the ordinary thiosulphate method. If very much iron is present, this treatment will not be sufficient and the iron precipitate after the second filtration must be twice oxidized again, filtered and the filtrate added to the others.

Biological and Chemical Considerations of Hide and Pelt. I. The Relation of Elastins to the Tanning Process. W. MOELLER. *Coll.*, 1918, 105-117, and 125-137; *J. S. L. T. C.*, Sept., 1918. Pelt is not an individual protein. Elastin is the chief source of the sulphur in the hide although this has been doubted many times. Sulphureted hydrogen is evolved when elastin is treated with hydrochloric acid, hence less sulphur is found in elastin purified by means of acid. It is easily and completely desulphurized by treatment with alkali and the product has a slight swelling power which is not a property of untreated elastin. This desulphurization with alkalies distinguishes elastin from all other proteins which are only desulphurized with caustic potash. The inference is that the sulphur in elastin is loosely combined. The difference between elastin and collagen is reflected in the decomposition products: elastin giving 0.34 per cent. tyrosine. Although great difference of opinion rules with regard to the quantity of elastin in the hide, there is no doubt that it is considerable and not to be neglected in tannage. Possibly the elastin content depends very largely on the feeding and age of the animal, and the great variations in hides from different countries and breeds may be due to the elastins in the hide. Elastins can be microscopically detected in the hide by means of Weigert's solution or osmic acid. The elastic fibers are very similar to chamois leather fibers in both physical and chemical properties. They resist the action of boiling water and are only dissolved by boiling under pressure. They consist of extremely fine fibrils just as the collagen fibers. The properties of elastin point to its not being a single protein, but like leather, a colloidal complex which can contain different components in varying amount. This is borne out by the sulphur content, tyrosine content and the presence of oleic acid in elastin.

Elastin is more resistant to the action of acids and alkalies than collagen, but not to trypsin, hence the bating process separates the elastin fibers from the pelt. Liming results in the desulphurization of elastin and the saponification of its fatty constituents so that the delimed hide does not give the most important reactions of elastin. The elastic fibers can only be recognized after tannage in the case of certain kinds of leather. The elastins are not affected by the sweating process and during the tanning they are simply encased by the tanning material. The content of elastin and the change it undergoes in the preliminary processes is of great importance to the leather produced from different kinds of hides and in the author's opinion is one of the many unexplained causes why the quality and rendement of the leather is so dependent on the origin and quality of the raw hides. The high content of elastin is a great disadvantage, and it is the aim of the preliminary processes to remove as

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much as possible the indifference of the elastin without damaging the collagen fibers and to convert it into a compound more like collagen in its behavior towards tannins. The more completely this object is attained the greater will be the yield of leather and the better its quality. Those leathers which contain much unchanged elastin, as a result of insufficient preparatory treatment, have no great tensile strength because although unchanged elastin is very elastic this property does not show itself in the leather fiber.

Very strong criticism is made of Wood's remarks on the action of trypsin on collagen. Trypsin attacks elastin, but not collagen, hence a bated hide differs from a hide merely delimed with acid in containing no elastins. Fahrion has detected oleic acid in the scud from bated hides and in the author's opinion this is derived from the elastins digested during the bating process. The decomposition products of the elastins are particularly suitable for destroying the compounds of lime with the collagen. Together with this action the removal of the elastic fibers results in a complete change in the structure of the hide. Experiments are quoted in support of these statements.

(1) A delimed and bated hide, after being limed again, was no longer affected by bating because of the lack of elastins.
(2) On adding elastin and bating such a hide the process was very effective.
(3) The result was the same when a twice limed hide was treated with the hydrolytic products of elastin only.
(4) A twice limed hide was delimed with dilute mineral acid. There was no falling although the first bating had removed the elastin.

It is not the removal of lime or elastin, but the peptizing action of the decomposition products of elastin on the lime compounds which brings about falling.

Dog-fish Liver Oil. A. C. CHAPMAN. *Analyst,* 1918, 43, 156-158; *J. S. L. T. C.*, Sept., 1918. The liver of the common dog-fish (*Squalus acanthias*) yields, when minced and steamed, about 40-50 per cent. of its weight of a pale yellow oil, which becomes semi-solid at 10° C. owing to the separation of solid glycerides. Two specimens of the oil prepared from different batches of liver had the following physical and chemical characters, the analysis having been made after the oils had been cooled and the solid substance separated: Specific gravity at 15°/15° C., 0.9175, 0.9186; refractive index at 20° C., 1.4755, 1.4749; optical rotation in 100 mm. tube, —1.45; saponification value, 161.0, 168.3; iodine value (Wijs), 123.3, 123.0; free fatty acids (as oleic acid), 0.33, 0.42 per cent.; unsaponifiable matter, 32.94, 9.48 per cent.; brominated glycerides insoluble in ether, 19.25, 24.95 per cent. The proportion of unsaponifiable matter in the oil appears to depend on the age and condition of the fish.

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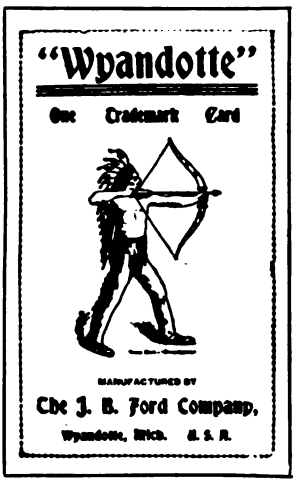

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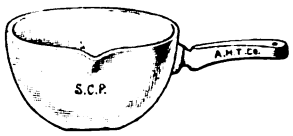

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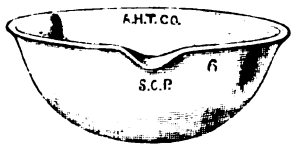

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